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# Towards the Development of a Fundamentally-based Chemical Model for Cyclopentanone: High Pressure Limit Rate Constants for H-atom Abstraction and Fuel Radical Decomposition

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## Abstract

Theoretical aspects of the development of a chemical kinetic model for the pyrolysis and combustion of a cyclic ketone, cyclopentanone, are considered. Calculated thermodynamic and kinetic data are presented for the first time for the principal species including 2- and 3-oxo-cyclopentyl radicals which are in reasonable agreement with the literature. These radicals can be formed via H-atom abstraction reactions by  $\dot{\text{H}}$  and  $\dot{\text{O}}$  atoms, and  $\dot{\text{O}}\text{H}$ ,  $\text{H}\dot{\text{O}}_2$ , and  $\dot{\text{C}}\text{H}_3$  radicals, the rate constants of which have been calculated. Abstraction from the  $\beta$  hydrogen atom is the dominant process when  $\dot{\text{O}}\text{H}$  is involved but the reverse holds true for  $\text{H}\dot{\text{O}}_2$  radicals. The subsequent  $\beta$ -scission of the radicals formed are also determined and it is shown that recent tunable VUV photoionization mass spectrometry experiments can be interpreted in this light. The bulk

13 of the calculations used the composite model chemistry G4 which was benchmarked in  
14 the simplest case with a coupled cluster treatment, CCSD(T), in the complete basis  
15 set limit.

## 16 Introduction

17 Bio-derived fuels can be used to displace fossil fuels in practical combustion devices to lower  
18 greenhouse-gas emissions. Cyclopentanone is a ketone that can be bio-derived because this  
19 chemical class is formed when fungi break down cellulose, a major component of biomass.<sup>1,2</sup>  
20 Moreover, cyclopentanone is a component in mixtures formed from the pyrolysis of biomass,  
21 for example, during the fast pyrolysis of aspen wood chips.<sup>3</sup>

22 Cyclopentanone has fuel properties that are attractive for applications in spark-ignition  
23 internal-combustion engines. It has the lowest autoignition reactivity of a number of biofu-  
24 els.<sup>4</sup> These properties make cyclopentanone especially attractive as a blending component for  
25 use in boosted spark-ignition engines because of its resistance to autoignition. Downsized,  
26 boosted spark-ignition engines are an attractive technology that allows higher efficiencies  
27 than most current spark-ignition engines in the light-duty ground transportation market.<sup>5</sup>  
28 This means cyclopentanone is not only attractive because it can be bio-derived, but also  
29 because its properties allow gains in engine efficiency; both of these characteristics yield po-  
30 tential reductions in greenhouse gas emissions. Cyclopentanone forms dimers<sup>6</sup> through quite  
31 weak hydrogen bond interactions C–H...O which probably accounts for its higher density  
32 and boiling point in comparison to the acyclic diethyl ketone.

33 Engine simulations can be used to assess the potential of cyclopentanone as a blending  
34 agent in gasoline, but these require a chemical kinetic model to simulate its ignition proper-  
35 ties; such a mechanism is not currently available. The mechanism needs to be valid for use in  
36 predicting combustion in both spark ignition and compression ignition engines. This means  
37 the mechanism should be predictive for end-gas autoignition and flame speed, and ignition  
38 phasing in a homogeneous-ignition compression-ignition engine. To achieve this predictivity,

39 it is recommended that the mechanism should be valid for conditions of pressure from 3  
40 to 50 atm, at temperatures from 600 K to 1500 K, at a dilution of up to 20% (by exhaust gas  
41 recirculation) and at equivalence ratios of 0.5 to 1.0. The objective of this work is to provide  
42 rate constants and product channels needed to support the development of a chemical kinetic  
43 mechanism for cyclopentanone.

44 The molecular reactions of a six-membered cyclic ketone, cyclohexanone, has been stud-  
45 ied by Zaras et al.<sup>7</sup> at the G3B3 level of theory. In a companion experimental work on  
46 cyclohexanone oxidation in a jet-stirred reactor they discuss qualitatively the fate of the  
47 three radicals produced by H-atom abstraction from the parent ketone.<sup>8</sup>

48 To achieve predictability, accurate rate constants are needed. At low and intermediate  
49 temperatures where autoignition reactions occur, chemical kinetic mechanisms for fuels are  
50 particularly sensitive to H-atom abstraction rates by  $\dot{\text{O}}\text{H}$  and  $\text{H}\dot{\text{O}}_2$  radicals. Providing accu-  
51 rate rate constants for these reactions will contribute to the prediction of engine knock. For  
52 flame speed predictions, accurate rate constant of hydrogen atom abstraction by hydrogen  
53 atoms may also be helpful. Additionally, the decomposition rate constants for fuel radicals  
54 formed from these hydrogen-atom abstraction reactions are also needed in high temperature  
55 fuel reactivity predictions. The decomposition of a cyclopentanone radical is more compli-  
56 cated than that of the much-studied acyclic alkyl radical, and involves the opening of a ring  
57 containing a ketone group. It is difficult to estimate its rate constant by analogy to other  
58 radical decompositions whose rate constants are available in the literature.

59 Zaras et al.<sup>9</sup> have calculated barrier heights for the decomposition of cyclopentanone at  
60 the G3B3 level of theory and also calculate accompanying rate constants. Low temperature  
61 oxidation pathways of cyclic ketones have been explored by Scheer et al.<sup>10</sup> who focused pri-  
62 marily on the subsequent reactions of the initial radicals with oxygen. Furthermore, Xia and  
63 colleagues<sup>11</sup> have reported on the excited-state ring-opening mechanisms of cyclic ketones  
64 including cyclopentanone without further investigation of the ring-opening rate constants.

65 In this paper, rate constants for H-atom abstraction from cyclopentanone by  $\dot{\text{O}}\text{H}$ ,  $\text{H}\dot{\text{O}}_2$

66 and  $\dot{\text{C}}\text{H}_3$  radicals and  $\dot{\text{H}}$  and  $\ddot{\text{O}}$  atoms are calculated using ab initio methods. In addition  
67 the rate constants for cyclopentanone radical decompositions are also computed. These key  
68 rate constants and their associated product channels will help towards the development of a  
69 detailed chemical kinetic mechanism to describe cyclopentanone oxidation.

## 70 Computational methodology

71 Optimized geometries, frequencies, international rotational potentials, and energies of the  
72 stable complexes and saddle points along the intrinsic reaction coordinate (IRC) were calcu-  
73 lated at the M062X/6-311++G(d,p) level of theory.<sup>12</sup> Geometry optimization was followed  
74 by vibrational frequency analysis to verify the local minima (number of imaginary frequen-  
75 cies equal to zero) or first order saddle points (number of imaginary frequencies equal to  
76 one) character of the compounds. Intrinsic reaction coordinate (IRC) calculations<sup>13,14</sup> are  
77 carried out to calculate the connection between transition states and the reactant or product  
78 complexes.

To achieve more reliable energies of the various species along the potential energy sur-  
faces, we have employed the CCSD(T) (coupled-cluster approach with single and double  
substitutions including a perturbative estimate of connected triples substitutions) method  
with the correlation-consistent polarized split-valence multiple- $\zeta$  basis sets, cc-pVTZ, and  
cc-pVQZ<sup>15</sup> for hydrogen abstraction by  $\dot{\text{O}}\text{H}$  radicals. The CCSD(T) total energies were ex-  
trapolated to the complete basis set (CBS) limit according to the procedure of Halkier *et*  
*al.*:<sup>16</sup>

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

79 where  $X = 4$  for the cc-pVQZ basis set. All the single point energy calculations mentioned  
80 above are based on the M062X/6-311++G(d,p) geometries. The  $T_1$  diagnostics for pre- and  
81 post- reaction complexes and transition states are all lower than the critical 0.02 value, and  
82 so that single-reference methods are expected to give an adequate description of the wave

83 function.<sup>17</sup> Single point energy calculations using the CCSD(T) method were carried out  
84 using the Molpro program.<sup>18</sup> The CCSD(T)/CBS methodology is computationally expensive  
85 and sometimes failed to converge, so only certain key processes were undertaken at this level  
86 of theory in order to benchmark the G4 method which was used for all of the electronic  
87 energy calculations in this work.<sup>19</sup> Electronic structure calculations were performed using  
88 the Gaussian-09<sup>20</sup> application.

89 The zero-point corrected electronic energies barrier heights using the G4 method were  
90 used in conjunction with scaled frequencies and rotational constants to calculate the high-  
91 pressure limit rate constants in the temperature range of 500–2000 K. The low-frequency  
92 torsional modes were treated as hindered rotors using a Pitzer-Gwinn-like approximation  
93 except for those transition states involving abstraction by a methyl radical where a free  
94 rotor approximation was used due to the very low rotational barrier. The hindrance po-  
95 tentials were determined for every geometry around all possible dihedral angles by fitting  
96 Fourier series to the M062X/6-311++G(d,p) energies along the relaxed internal rotation.  
97 The remaining conserved modes were treated as harmonic oscillators. Eckart asymmetric  
98 tunneling corrections were included.<sup>21</sup> Variflex and Multiwell were used to carry out these  
99 rate coefficient calculations.<sup>22–24</sup> The thermochemical calculations were performed using the  
100 Thermo module of Multiwell.

## 101 **RESULTS AND DISCUSSION**

### 102 **Geometry of cyclopentanone**

103 Cyclopentanone (CPO) is a non-planar five membered ring with C<sub>2</sub> symmetry and the  
104 labelled structure is shown in Fig. 1; Cartesian coordinates, vibrational frequencies and  
105 rotational constants for CPO and other species are provided in the Supplemental Material.  
106 The hydrogen atoms occupy positions which may be loosely described as ‘equatorial’ (eq)  
107 and ‘axial’ (ax) at both the  $\alpha$ -carbons adjacent to the ketonic group, C2 and C5, and the

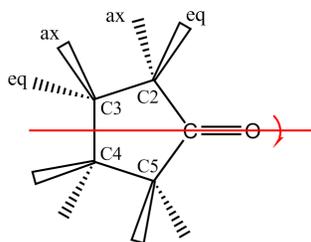


Figure 1: Cyclopentanone

108  $\beta$ -carbons, C3 and C4, which are more remote.

109 The C–H bond dissociation energies at 298.15 K are  $C_\alpha\text{–H} = 379$  and  $C_\beta\text{–H} = 407$   
 110  $\text{kJ mol}^{-1}$  in satisfactory agreement with the corresponding values of 382 and 411  $\text{kJ mol}^{-1}$   
 111 computed by Zaras et al.<sup>9</sup> (except that these refer to 0 K) and the CBS-QB3 values<sup>10</sup> of  
 112 378 and 407  $\text{kJ mol}^{-1}$ . These values are to be compared to that for cyclopentane<sup>25</sup> where  
 113  $\text{C–H} = 400 \pm 4 \text{ kJ mol}^{-1}$ .

114 The enthalpy of formation at 298.15 K of  $-194.8 \pm 6.4 \text{ kJ mol}^{-1}$ , calculated by an atom-  
 115 ization procedure,<sup>26</sup> is in good agreement with the most recent experimental determination<sup>27</sup>  
 116 by reductive calorimetry of  $-197.4 \pm 1.3 \text{ kJ mol}^{-1}$  and with much earlier static bomb com-  
 117 bustion calorimetric measurements of  $-194.8 \pm 1.7$  and  $-193.0 \pm 1.8 \text{ kJ mol}^{-1}$  by Wolf<sup>28</sup>  
 118 and Sellers and Sunner.<sup>29</sup> The computed constant pressure heat capacity of gaseous CPO of  
 119  $96.4 \text{ J K}^{-1} \text{ mol}^{-1}$  is in good agreement with the literature value<sup>30</sup> of  $95.33 \text{ J K}^{-1} \text{ mol}^{-1}$ .

120 The  $\Delta_f H^\circ(298.15 \text{ K})$  of 2-oxo-cyclopentyl (CPO-2) and 3-oxo-cyclopentyl (CPO-3) rad-  
 121 icals have been calculated and they are  $-28.8$  and  $-0.4 \text{ kJ mol}^{-1}$ , respectively, with CPO-2  
 122 being considerably more stable because of the resonance stabilization of the  $\text{CH}\dot{\text{C}}\text{=O}$   
 123 moiety.

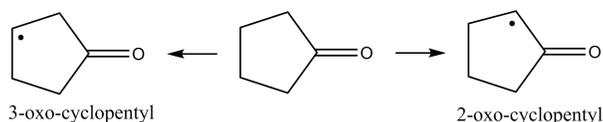


Figure 2: Cyclopentanone and its radicals

## 124 H-atom abstraction by $\dot{\text{O}}\text{H}$ radical

125 Hydrogen atom abstraction reactions lead to the formation of the two oxo-cyclopentyl rad-  
126 icals as shown in Fig. 2. There are only four different abstractable H-atoms which can be  
127 described as ‘equatorial’ and ‘axial’ attached to  $\alpha$ - and  $\beta$ -carbons. Table 1 lists the G4  
128 zero-point corrected electronic energies of the pre- and post-reaction complexes, the transi-  
129 tion states and the final products, all relative to the reactants. For the reaction channels  
130 involving the formation of van der Waals pre-reaction complexes, the rate constant for that  
131 reaction channel is determined by two reaction steps which are the formation of a weakly  
132 bound van der Waals complex and a H-atom abstraction step with a tight transition state.

133 Georgievskii and Klippenstein<sup>31</sup> have proposed a two transition state model to study the  
134 kinetics of the  $\text{C}_2\text{H}_6 + \dot{\text{C}}\text{N}$  reaction and stated that, for those two step transition state reac-  
135 tion processes, the outer transition state forming the van der Waals complex is important and  
136 should be taken into consideration using variational transition state theory for temperatures  
137 lower than 300 K. However, for temperatures higher than 300 K, a single inner transition  
138 state description can be used for computing the rate constant. In *this work* the temperature  
139 range of interest is 500–2000 K so the kinetics of the formation of pre-reaction complexes  
140 has been neglected.

141 Electronic energies for the barriers of  $\alpha$  eq,  $\alpha$  ax, and  $\beta$  ax have also been calculated at  
142 the CCSD(T)/CBS level of theory, and the comparison with G4 results is shown in Table 1;  
143 the difference between those two methods ranges from 5.6 to 1.2 kJ mol<sup>-1</sup> which is still  
144 within the uncertainty of the electronic energy calculations. The CCSD(T)/CBS energies  
145 are not shown for the  $\beta$  eq site because the electronic energy calculation for the transition  
146 state did not converge.

147 Typically H-atom abstraction from oxygenates by  $\dot{\text{O}}\text{H}$  radicals involves the formation  
148 of weakly-bound pre- and post-reaction complexes and this system is no exception; Fig. 3  
149 shows a schematic of abstraction from the ‘equatorial’ hydrogen at an  $\alpha$ -carbon. The zero  
150 point energies of the pre- and post-reaction energies are shown in Table 1, while no pre- or

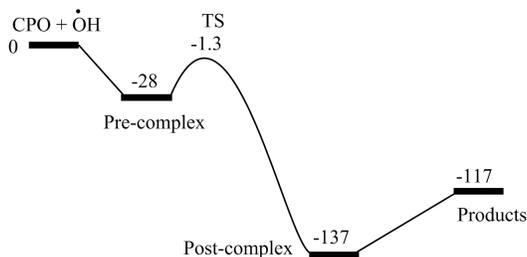


Figure 3: Potential energy surface for channel  $\alpha$  eq,  $\text{kJ mol}^{-1}$  at G4 level of theory (0 K).

151 post- reactions complexes were found for the  $\beta$  eq site. The stabilisation of the pre-reaction  
 152 complex, relative to the reactants, amounts to  $28 \text{ kJ mol}^{-1}$  and that of the post-reaction  
 153 complex, relative to the final products, is  $20 \text{ kJ mol}^{-1}$ . This is typical of values encountered  
 154 in many similar systems as recorded by Galano and colleagues.<sup>32</sup>

155 Tunneling, evaluated with the Eckart model, plays a role in these reactions and cannot  
 156 be ignored for temperatures lower than 1000 K. Taking the reaction channel  $\alpha$  eq as an  
 157 example, the rate constant ratio with/without tunneling is 1.8 at 500 K and decreases to 1.2  
 158 at 1000 K.

Table 1: Zero-point corrected electronic energies at G4 and (CCSD(T)/CBS) /  $\text{kJ mol}^{-1}$

Site	Pre-	TS	Post-	Prod.
H-abstraction by $\dot{\text{O}}\text{H}$ radical				
$\alpha$ eq	-28.1	-1.26 (4.32)	-137.3	-116.7 (-111.7)
$\alpha$ ax	-28.1	4.10 (1.21)	-137.3	-116.7 (-111.7)
$\beta$ eq	—	4.10	—	-89.6 (-86.0)
$\beta$ ax	-28.1	0.62 (-0.15)	-98.0	-89.6 (-86.0)
H-abstraction by $\text{H}\dot{\text{O}}_2$ radical				
$\alpha$ eq	-47.5	63.3	-13.0	14.8
$\alpha$ ax	-47.6	57.3	-13.1	14.8
$\beta$ eq	-14.5	69.4	30.3	41.9
$\beta$ ax	-47.5	60.9	22.0	41.9

The high-pressure rate constants were obtained using the barrier heights computed by the G4 method because these computations were tractable for all the reactions considered in this work. For H-atom abstraction by  $\dot{\text{O}}\text{H}$  radicals from the adjacent or  $\alpha$ -carbon atoms C2 and C5 to yield the CPO-2 radical the total rate constant is calculated to be, in  $\text{cm}^3 \text{ mol}^{-1}$

s<sup>-1</sup>:

$$k_{\alpha} = 2.34 \times 10^3 T^{3.04} \exp(817/T)$$

and that from the remote  $\beta$ -carbon atoms C3 and C4 to give CPO-3:

$$k_{\beta} = 1.13 \times 10^5 T^{2.58} \exp(626/T)$$

159 Thus, over the fitting range of 500–2000 K abstraction predominantly occurs from the  $\beta$   
160 positions decreasing slightly as the temperature increases, Fig. 4a.

161 There is no data in the literature against which these calculations can be tested except  
162 for a single room temperature measurement by Dagaut et al.,<sup>33</sup> using a flash photolysis  
163 resonance fluorescence technique, who reported  $k = (1.77 \pm 0.11) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  with  
164 the corresponding value obtained *here* of  $k_{\alpha} + k_{\beta} = 3.51 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  with this  
165 prediction being a factor of two faster than that measured by Dagaut et al.<sup>33</sup>

166 Abstraction from the  $\beta$  carbon atoms is always faster than from the  $\alpha$  carbon atoms,  
167 Fig. 4a. Even though the reaction barrier is 1.9 kJ mol<sup>-1</sup> lower for the  $\alpha$  eq position; the  
168  $\alpha$  ax and  $\beta$  eq hydrogen atoms have the same barriers and the rate constant are almost  
169 identical in the entire temperature range.

170 Rate constants for the  $\beta$  axial channel are about a factor of 2.5 higher than the  $\alpha$   
171 equatorial channel, Fig. 4b. A comparison of the relaxed potential energy scans for the  
172 C $\cdots$ H $\cdots$ O—H internal rotor for the two relevant transition states shows a significant differ-  
173 ence, Fig. 5. The reaction channel forming an  $\alpha$  equatorial radical is about 16 kJ mol<sup>-1</sup>  
174 which is typical of a hindered rotor but for the  $\beta$  axial reaction channel it is only 2.5 kJ  
175 mol<sup>-1</sup> — effectively a free rotor. The root cause of the difference is the interaction that  
176 occurs as the hydrogen atom in the OH group moves closer to the ketonic oxygen, forming  
177 in essence a six-membered ring system.

178 In summary, the hydrogen bond formed in the transition state leads to a relatively stable  
179 six-membered-ring structure and thereby lowers the barrier height but also lowers the entropy

180 of that reaction channel. The final rate constants are determined by the competition between  
 181 these two parameters, and in this case the entropy terms dominates and  $k_\alpha$  equatorial is  
 182 smaller than  $k_\beta$  axial.

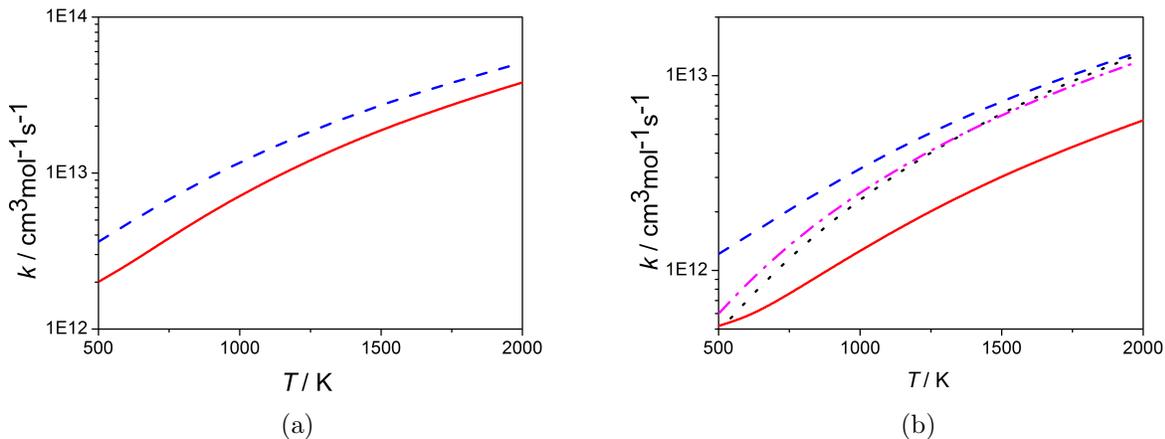


Figure 4: (a) Total rate constants for H-abstraction by  $\dot{\text{O}}\text{H}$  radical from CPO to form CPO-2 (—) and CPO-3 (---). (b) Single channel rate constant (per H-atom) for hydrogen abstraction by  $\dot{\text{O}}\text{H}$  radical from CPO.  $\alpha$  eq —,  $\beta$  ax ---,  $\alpha$  ax  $\cdots$ ,  $\beta$  eq, - · -.

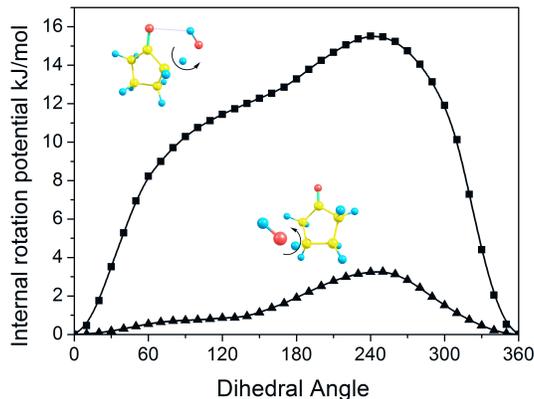


Figure 5:  $\text{C}\cdots\text{H}\cdots\text{O}-\text{H}$  internal rotor in transition states:  $\blacksquare$   $\alpha$  eq,  $\blacktriangle$   $\beta$  ax.

183 Chemical kinetic rate constants depend upon both geometry and frequency calculations  
 184 since these determine the rotational and vibrational partition functions. Two sets of fre-  
 185 quency modes and rotational constants have been calculated at the B3LYP/6-311(2df,p)  
 186 (the geometry optimizer in G4 theory) and M062X/6-311++G(d,p) levels of theory for both

187 reactants and transition state for the  $\alpha$  eq channel. However the difference between the final  
188 rate constants from these two approaches is negligible, with a maximum difference of only  
189 3.5%, Fig. S3. Thus, the uncertainty in the rate constants arising from different approaches  
190 to determine the partition functions can be neglected.

## 191 H-atom abstraction by $\text{HO}_2$ radical

192 As observed for the  $\dot{\text{O}}\text{H}$  radical, the hydroperoxyl radical forms both pre- and post-reaction  
193 complexes which are typically more stabilized, Fig. 6. However, there are differences: the  
194 hydroperoxyl radical abstraction reaction has higher barriers which lie above the entrance  
195 channel and has endothermic rather than exothermic products. Relative electronic energies  
196 for pre-reaction complexes, transition states and post-reaction complexes are also shown  
197 in Table 1. All of the electronic energies for the H-atom abstraction by  $\text{HO}_2$  radicals are  
198 reported at the G4 level of theory in this work.

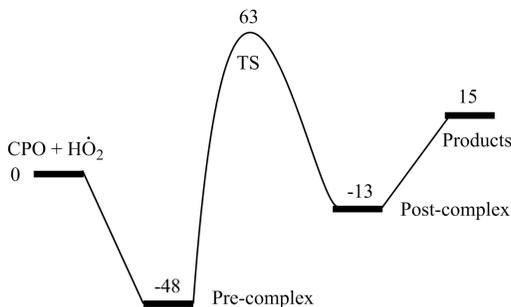


Figure 6: Potential energy surface for channel  $\alpha$  eq,  $\text{kJ mol}^{-1}$  at G4 level of theory (0 K).

199 A comparison of the internal rotation of the  $\text{HO}_2$  fragment in the transition states of  $\alpha$   
200 equatorial and  $\beta$  equatorial is shown in Fig. 7. As previously, there is a difference because of  
201 the interaction of  $\text{OOH}$  with the ketonic oxygen although this time a seven-membered ring  
202 is formed. However, the difference is not as pronounced as was the case for  $\dot{\text{O}}\text{H}$  abstraction  
203 and this is reflected in the computed rate constants.

204 Total rate constants for abstraction by  $\text{HO}_2$  radicals are calculated to be (in units of  $\text{cm}^3$

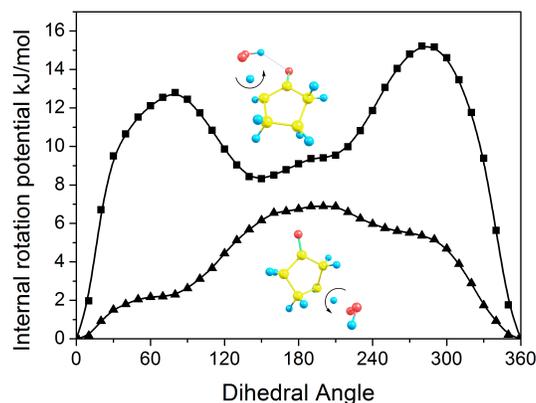


Figure 7: H $\cdots$ O—O—H hindered rotor in transition states:  $\blacksquare$   $\alpha$  eq, and  $\blacktriangle$   $\beta$  eq.

205 mol $^{-1}$  s $^{-1}$ ):

$$k_{\alpha} = 9.91 \times 10^{-4} T^{4.74} \exp(-5,040/T)$$

$$k_{\beta} = 5.45 \times 10^{-2} T^{4.27} \exp(-5,957/T)$$

206 For abstraction by HO $\dot{O}_2$  radicals twice as much 2-oxo-cyclopentyl radical is formed at  
 207 500 K in comparison to the 3-oxo radical; this ratio diminishes with increasing temperature  
 208 until it approaches unity at 1800 K.

## 209 H-atom abstraction by $\dot{H}$ and $\ddot{O}$ atoms and $\dot{C}H_3$ radicals

210 Barriers and reaction energies as well as site-specific rate constants (sum of the rate constants  
 211 for abstracting the same type of hydrogen atom) in a modified Arrhenius format are shown  
 212 in Table 2 for H-atom abstraction from CPO by  $\dot{H}$  and  $\ddot{O}$  atoms and  $\dot{C}H_3$  radicals. The  
 213 values obtained for abstraction by  $\dot{H}$  atoms are comparable to those for tetrahydrofuran  
 214 (THF) although these were computed at a different level of theory.<sup>34</sup> The  $\alpha$ -carbon positions  
 215 are somewhat more reactive than the  $\beta$ -carbons but the differences are slight.

216 For H-atom abstraction by  $\dot{C}H_3$  radicals, the rate constant for the  $\alpha$  channel is faster than  
 217 that for the  $\beta$  channel over the entire temperature range investigated here (500 – 2000 K),

218 Fig. 8a. Rate constants for both channels are faster than for abstraction of the secondary  
219 hydrogen atom in an *n*-alkane provided by Manion et al.<sup>35</sup> The electronic energy barrier  
220 heights for abstraction of the  $\beta$  hydrogen atom are  $6.8 \text{ kJ mol}^{-1}$  ( $\beta$  eq) and  $11.5 \text{ kJ mol}^{-1}$  ( $\beta$   
221 ax) *lower* than abstraction of the  $\beta$  H-atom in THF and the rate constant from the CPO-3  
222 ( $\beta$ ) site is faster than for the  $\beta$  site in THF.

223 For H-atom abstraction by  $\dot{\text{H}}$  atoms, the  $\alpha$  rate constant is faster than the  $\beta$  rate constant  
224 at temperatures below 2000 K, Fig. 8b. The  $\alpha$  rate constant is close to the rate for H-atom  
225 abstraction in cyclopentane.<sup>36</sup> The rate constant of hydrogen atom abstraction from the  
226 CPO-3 ( $\beta$ ) site is about 10 times lower at 900 K than the analogous C3 or  $\beta$ -carbon site in  
227 THF.

228 It is interesting to note that in the case of H-atom abstraction by  $\ddot{\text{O}}$  atoms, Fig. 8c, the  
229 rate constants of the  $\alpha$  pathway are lower than that for the  $\beta$  pathway even though the C–H  
230 bond strength at the  $\alpha$  site is much weaker. The  $\alpha$ -transition states are ‘early’ whilst the  
231  $\beta$ -transition states are ‘late’ viewed from the perspective of the C $\cdots$ H and the H $\cdots$ O bond  
232 distances, viz.  $\alpha$  1.23 and 1.31 versus  $\beta$  1.27 and 1.25 Å. The abstraction rate constant from  
233 the  $\beta$  site of CPO is within a factor of two of reported rate constants for secondary sites in  
234 *n*-alkanes.<sup>37,38</sup>

## 235 Fate of cyclopentanone radicals

236 The 2-oxo-cyclopentyl radical is more stable than the 3-oxo isomer and the equilibrium  
237 constant approaches unity only at 1,850 K. Interconversion via a 1,3 hydrogen shift reaction  
238 is feasible with a barrier of  $167 \text{ kJ mol}^{-1}$  with an isomerization rate constant calculated to  
239 be  $2.66 \times 10^{13} \exp(-20,393/T) \text{ s}^{-1}$ . The half-life of a CPO-2 radical isomerizing to CPO-  
240 3 therefore is approximately 1  $\mu\text{s}$  at 1,050 K. As will be evident below isomerization is  
241 slower than the competitive ring-opening reaction RO2 available to CPO-2. In a similar  
242 vein isomerization of 3-oxo to 2-oxo is *slower* than the corresponding fastest ring-opening  
243 reaction RO4.

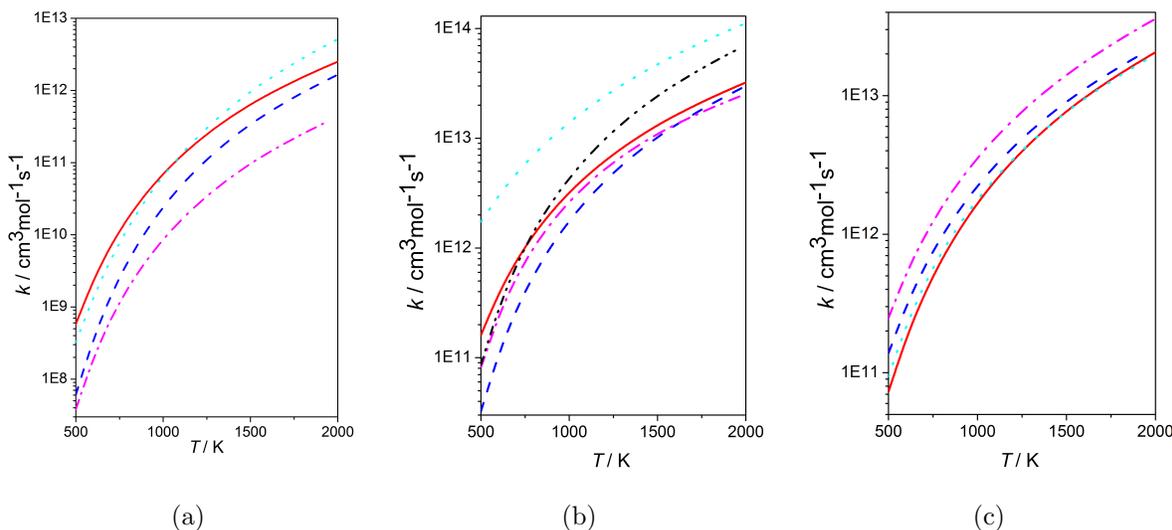


Figure 8: (a) H-abstraction by  $\dot{\text{C}}\text{H}_3$  radicals from CPO to form CPO-2 (—), CPO-3 (---), from a  $\beta$  site in THF<sup>34</sup> (···) and from  $-\text{CH}_2-$  in an  $n$ -alkane<sup>35</sup> (-·-). (b) H-abstraction by  $\dot{\text{H}}$  atom from CPO to form CPO-2 (—) and CPO-3 (---), from  $\beta$  site in THF<sup>34</sup> (···), cyclopentane (-·-), from  $-\text{CH}_2-$  in an  $n$ -alkane<sup>36</sup> (-·-). (c) H-abstraction by  $\ddot{\text{O}}$  atom from CPO to form CPO-2 (—), CPO-3 (---), from  $-\text{CH}_2-$  in an  $n$ -alkane (···),<sup>37</sup> (-·-)<sup>38</sup>

Table 2: H-abstraction by  $\dot{\text{H}}$ ,  $\ddot{\text{O}}$  and  $\dot{\text{C}}\text{H}_3$ ; units kJ, mol, s; rate constants are for per H-atom

Site	$E^\ddagger$	$\Delta_r H$	$A$ -factor	$n$	$E_A$
$\dot{\text{H}}$ atom					
$\alpha$ eq	27.3	-60.9	$2.64 \times 10^6$	2.185	18.1
$\alpha$ ax	20.0	-60.9	$3.39 \times 10^6$	2.121	10.8
$\beta$ eq	34.2	-33.8	$2.05 \times 10^6$	2.259	24.6
$\beta$ ax	28.1	-33.8	$1.71 \times 10^6$	2.263	18.5
$\ddot{\text{O}}$ atom					
$\alpha$ eq	21.6	-54.0	$2.09 \times 10^5$	2.501	15.8
$\alpha$ ax	14.5	-54.0	$1.33 \times 10^5$	2.389	8.6
$\beta$ eq	18.2	-26.9	$5.14 \times 10^4$	2.629	10.9
$\beta$ ax	13.4	-26.9	$7.03 \times 10^4$	2.522	6.6
$\dot{\text{C}}\text{H}_3$ radical					
$\alpha$ eq	38.8	-57.6	$5.49 \times 10^1$	3.270	25.2
$\alpha$ ax	32.1	-57.6	$3.38 \times 10^1$	3.232	18.7
$\beta$ eq	49.4	-30.5	$8.48 \times 10^0$	3.483	33.2
$\beta$ ax	44.7	-30.5	$9.69 \times 10^0$	3.468	28.7

244 The initially formed CPO-2, and CPO-3 radicals can undergo  $\beta$ -scission reactions; thus,  
 245 CPO-2 can ring-open via C3-C4 and C5-C1 scission, Fig. 9, whilst CPO-3 faces a similar  
 246 choice between C4-C5 and C2-C1, Fig. 10. The computed barrier heights, in  $\text{kJ mol}^{-1}$ , for  
 247 reactions RO1-RO4 are in reasonable agreement with those calculated by Scheer et al.<sup>10</sup>

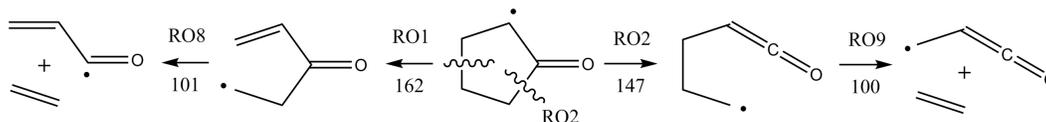


Figure 9: Reaction barriers of 2-oxo-cyclopentyl,  $\text{kJ mol}^{-1}$ .

248 Subsequent reactions of RO8, RO9 and RO5, RO7 produce species whose chemistry is  
 249 somewhat better known; an additional channel RO6 is in competition with RO7 and leads to  
 250 the same products as channel RO5, namely allyl radical + ketene but faces a larger barrier  
 251 of  $69 \text{ kJ mol}^{-1}$ .

252 The calculated Arrhenius parameters for these reactions are listed in Table 3 from which  
 253 it can be inferred that scission of the C1-C2 or C1-C5 bonds prevails over scission of the  
 254 C3-C4 bond, that is  $k(\text{RO2}) > k(\text{RO1})$  and  $k(\text{RO4}) > k(\text{RO3})$  and the elimination of CO  
 255 is much faster than the formation of allyl and ketene,  $k(\text{RO7}) \gg k(\text{RO6})$ . Thus, the 3-  
 256 oxo-cyclopentyl radical is more reactive and in the absence of other interfering reactions will  
 257 primarily decompose by elimination of carbon monoxide to yield the 3-buten-1-yl radical,  
 258  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\dot{\text{C}}\text{H}_2$ . Subsequent reactions of this radical, such as a 1,2-hydrogen shift to  
 259 form an allylic system,  $\text{H}_2\text{C}::\dot{\text{C}}\text{H}::\text{CH}_2\text{CH}_3$ , have been thoroughly explored in recent times  
 260 by Dean et al.<sup>39</sup> and Miyoshi.<sup>40</sup>

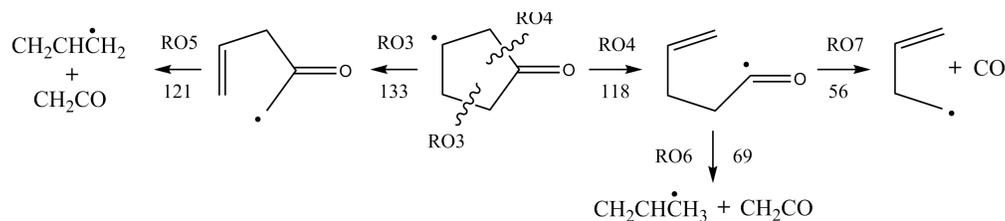


Figure 10: Reactions of 3-oxo-cyclopentyl /  $\text{kJ mol}^{-1}$ .

261 We note that species corresponding to  $\text{C}_4\text{H}_7^+$  were detected by mass spectrometry in

262 the very recent flow tube experiments<sup>10</sup> of  $\text{Cl}^\bullet + \text{CPO}$  at 550–650 K both in the presence  
263 *and* in the absence of  $\text{O}_2$ ; which is a supporting evidence of the essential correctness of the  
264 ring-opening and  $\beta$ -scission routes calculated here.

Table 3: Arrhenius parameters for ring opening.

#	$A$ -factor / $\text{s}^{-1}$	$E_A$ / $\text{kJ mol}^{-1}$
RO1	$1.32 \times 10^{14}$	169.5
RO2	$9.50 \times 10^{13}$	153.5
RO3	$1.39 \times 10^{13}$	138.1
RO4	$1.72 \times 10^{13}$	121.8
RO5	$3.92 \times 10^{13}$	127.1
RO6	$5.50 \times 10^{11}$	68.7
RO7	$6.08 \times 10^{14}$	65.1
RO8	$1.68 \times 10^{14}$	105.7
RO9	$5.69 \times 10^{13}$	104.6

265 In the Supplemental Material we have also compared the decomposition rate constants  
266 of RO1, RO2, RO3 and RO4 with similar reaction processes in the cyclopentane radical  
267 calculated by Wang<sup>41</sup> and Al Rashidi.<sup>42</sup>

## 268 Conclusions

269 The thermochemistry of cyclopentanone and its radicals has been computed. In addition,  
270 the C–H bond dissociation energies were also calculated to compare with existing literature  
271 values. Even though the comparisons do show some inconsistencies in the current literature,  
272 the discrepancy between the calculation in this work and the ones in the literature is still  
273 within  $4 \text{ kJ mol}^{-1}$ .

274 We have carried out a systematic detailed study of the energetics and chemical kinetics  
275 of the hydrogen atom abstraction reactions from cyclopentanone by  $\dot{\text{H}}$  and  $\ddot{\text{O}}$  atoms and  $\dot{\text{O}}\text{H}$ ,  
276  $\text{H}\dot{\text{O}}_2$  and  $\dot{\text{C}}\text{H}_3$  radicals.

277 For H-atom abstraction by  $\dot{\text{O}}\text{H}$  and  $\text{H}\dot{\text{O}}_2$  radicals, pre- and post-complexes were formed  
278 in most of the reaction channels especially for abstractions at the  $\alpha$  position.

279 The fate of the initially formed oxo-cyclopentyl radicals is delineated and it is shown that  
280 3-oxo-cyclopentyl is more reactive than 2-oxo-cyclopentyl, and consequently, in accordance  
281 with very recent observations, production of 3-buten-1-yl radical and CO is favored.

282 The results of this work are suitable for inclusion in present-day detailed chemical kinetic  
283 mechanisms, replacing estimated values which have been determined by analogy. However,  
284 there are other reaction classes, for example, the reaction of CPO-2 radical with  $\text{H}\dot{\text{O}}_2$  or  
285 of CPO-3 with molecular oxygen followed by subsequent isomerization and decomposition.  
286 These classes will be important in the low to intermediate temperature regimes, below 1000  
287 K. Further ab initio calculations for those reaction classes will be needed to determine the  
288 rate constants for these reactions and allow accurate predictions by chemical kinetic models.

289 For hydrogen abstraction by species not considered by the present study, such as  $\text{O}_2$  and  
290 other less important radicals, rate constants can be estimated by analogy to a secondary site  
291 in an *n*-alkene. In a similar vein other reactions will need to be estimated and/or computed  
292 in order to develop a comprehensive mechanism but the completion of this task and its  
293 validation against fundamental experimental data are beyond the scope of this work.

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## 302 **Supporting Information Available**

303 Supplementary data associated with this article is available in the online version. It includes  
304 the geometries, vibrational frequencies, rotational constants and energies of each species  
305 mentioned in the article. This material is available free of charge via the Internet at  
306 <http://pubs.acs.org/>.

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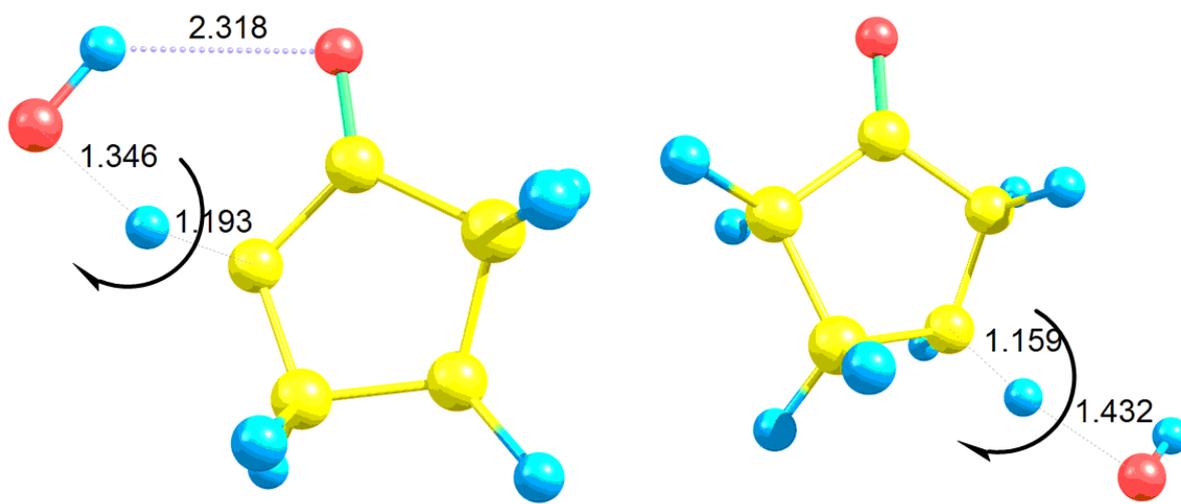


Fig: TOC graphic