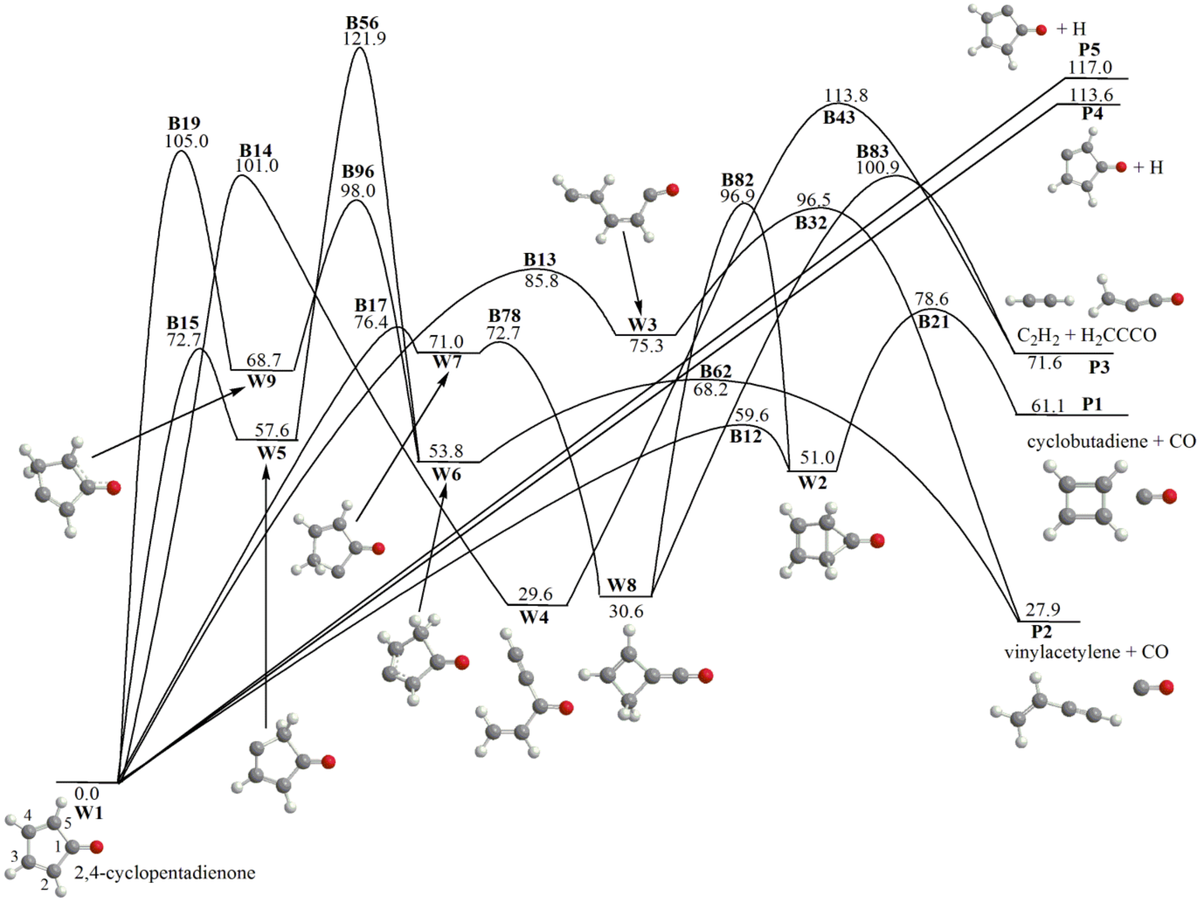
The reaction of pyrolysis of 2,4-cyclopentadienone C_5H_4O

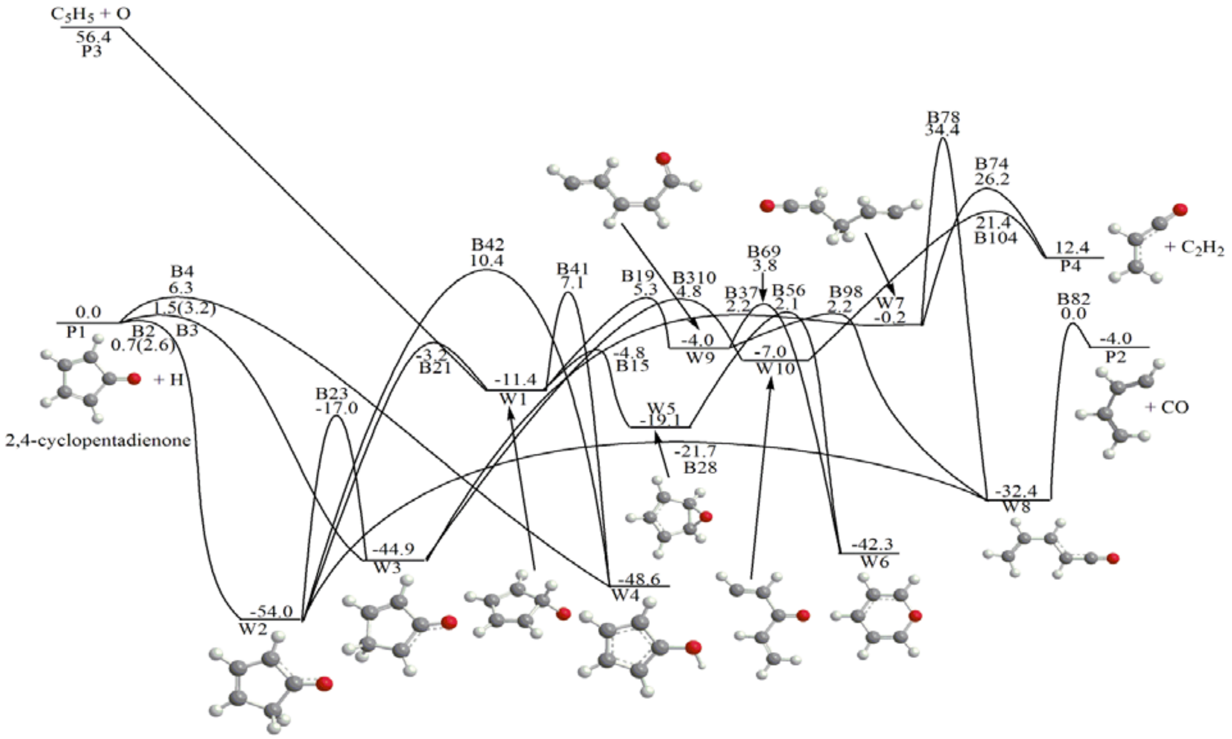
The important role of five-membered rings, as free radicals of cyclopentadienyl, and as embedded in huge molecules (acenaphthylene, indenyl), play an important role in combustion processes. In our works, the oxidation reactions of these systems by atomic and molecular oxygen and hydroxyl, are investigated. As the key reaction, initiating oxidation of the first aromatic ring, $C_6H_5 + O_2$ has drawn attention of many researchers. One of the major secondary five-member ring products detected in the $C_6H_5 + O_2$ reaction was 2,4-cyclopentadienone C_5H_4O. The potential energy surface (PES) for the pyrolysis of this compound is presented. The main products for the monomolecular decomposition are cyclobutadiene + CO. The rate constants for the main reaction products are presented in the table. The branching coefficients for $C_5H_4O \rightarrow$ vinylacetylene C_4H_4 + CO are 0,2%, 1,3%, 3,5% and 7,7% at 30 torr, 1,10 and 100 atm, respectively.



Reaction	*A*	α	*E*a	*k*(1500 K)
cyclopentadienone → cyclobutadiene + CO				
*k*30 Torr	3.32×10^{49}	-10.31	95.40	9.93×10^{2}
*k*1 atm	4.84×10^{38}	-6.95	91.39	2.82×10^{3}
*k*10 atm	5.46×10^{29}	-4.26	87.43	3.96×10^{3}
*k*100 atm	1.91×10^{23}	-2.33	84.44	4.40×10^{3}
cyclopentadienone → vinylacetylene + CO				
*k*30 Torr	1.80×10^{61}	-14.08	115.40	6.61×10^{-1}
*k*1 atm	6.70×10^{45}	-9.11	110.40	9.48
*k*10 atm	6.34×10^{35}	-5.94	107.50	27.1
*k*100 atm	1.36×10^{26}	-2.97	103.90	42.1

The C_5H_4O + H and C_5H_5+ O reactions

The obtained energies and geometries of the reagents, products and transition states and isomers for C_5H_4O + H and C_5H_5+ O are shown on the diagram of the PES. In the table are presented the Arrhenius expressions for the main rate constant values.



Reaction	*A*	α	*E*a	*k*(1500 K)
cyclopentadienone + H → C_4H_5 + CO				
$k_{30\ \text{Torr}}$	$1.87 \cdot 10^{17}$	-0.81	7.49	$3.87 \cdot 10^{13}$
$k_{1\ \text{atm}}$	$2.05 \cdot 10^{24}$	-2.72	13.91	$3.81 \cdot 10^{13}$
$k_{10\ \text{atm}}$	$8.82 \cdot 10^{28}$	-3.94	19.59	$3.60 \cdot 10^{13}$
$k_{100\ \text{atm}}$	$6.06 \cdot 10^{28}$	-3.75	24.01	$2.73 \cdot 10^{13}$
cyclopentadienone + H → C_3H_3O + C_2H_2				
$k_{30\ \text{Torr}}$	$7.57 \cdot 10^{15}$	-0.11	26.63	$4.52 \cdot 10^{11}$
$k_{1\ \text{atm}}$	$2.54 \cdot 10^{16}$	-0.26	27.08	$4.5 \cdot 10^{11}$
$k_{10\ \text{atm}}$	$1.07 \cdot 10^{20}$	-1.25	30.28	$4.46 \cdot 10^{11}$
$k_{100\ \text{atm}}$	$2.19 \cdot 10^{25}$	-2.63	37.11	$4.02 \cdot 10^{11}$
C_5H_5 + O → C_4H_5 + CO				
$k_{30\ \text{Torr}}$	$4.85 \cdot 10^{14}$	-0.26	5.56	$6.14 \cdot 10^{13}$
$k_{1\ \text{atm}}$	$4.87 \cdot 10^{14}$	-0.26	5.57	$6.14 \cdot 10^{13}$
$k_{10\ \text{atm}}$	$5.75 \cdot 10^{14}$	-0.28	6.18	$6.14 \cdot 10^{13}$
$k_{100\ \text{atm}}$	$8.43 \cdot 10^{14}$	-0.32	8.67	$6.11 \cdot 10^{13}$

At the combustion temperatures, the branching coefficient for cyclopentadienone + H → C_3H_3O + C_2H_2 do not exceed 14 %. For C_5H_5 + O the main products are butadienyl + CO (90+5%) at temperatures T=1500..2500 K.

Oxidation of Cyclopentadienyl Radical with Molecular Oxygen

The total reaction rate constants at all considered pressures merge at 1375 K and show no pressure dependence at higher temperatures where only the bimolecular products are formed. The reaction is predicted to be rather slow as the total rate constant exceeds the 10^{-15} cm^3 $molecule^{-1}$ s^{-1} threshold only at ~1600 K, with the highest value at 2500 K being 5.6×10^{-14} $molecule^{-1}$ s^{-1}. The present paper concludes a series of our works on the oxidation of cyclopentadienyl radical with oxygen containing species. Among the reactions of C_5H_5 with $O(^3P)$, OH, and O_2, the one with molecular oxygen is by far the slowest one.

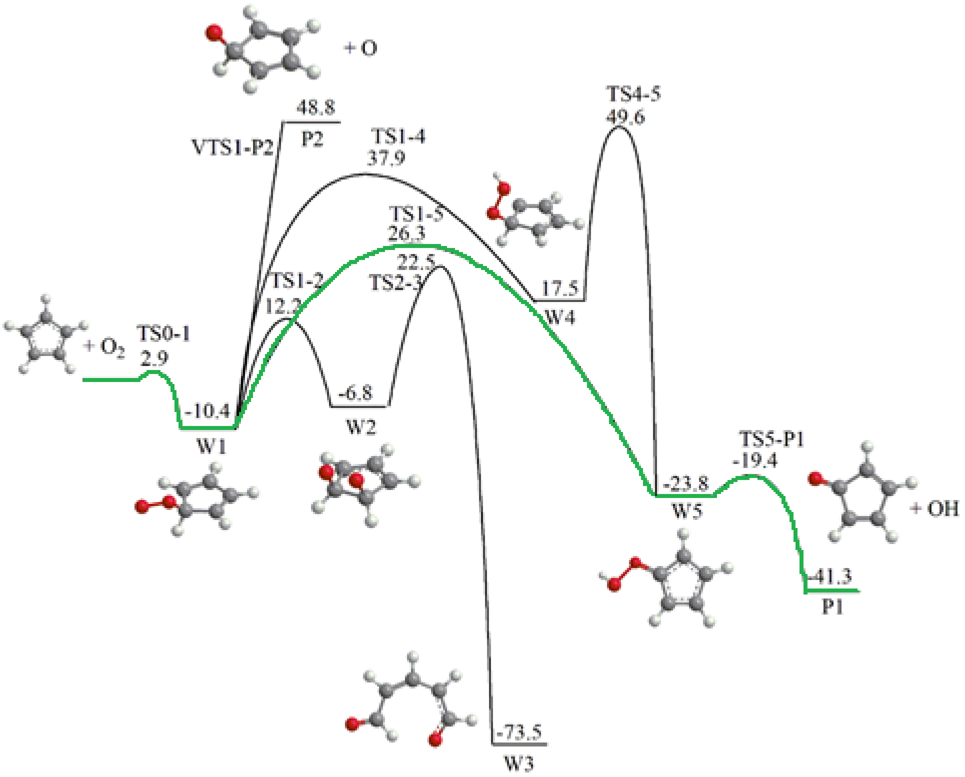
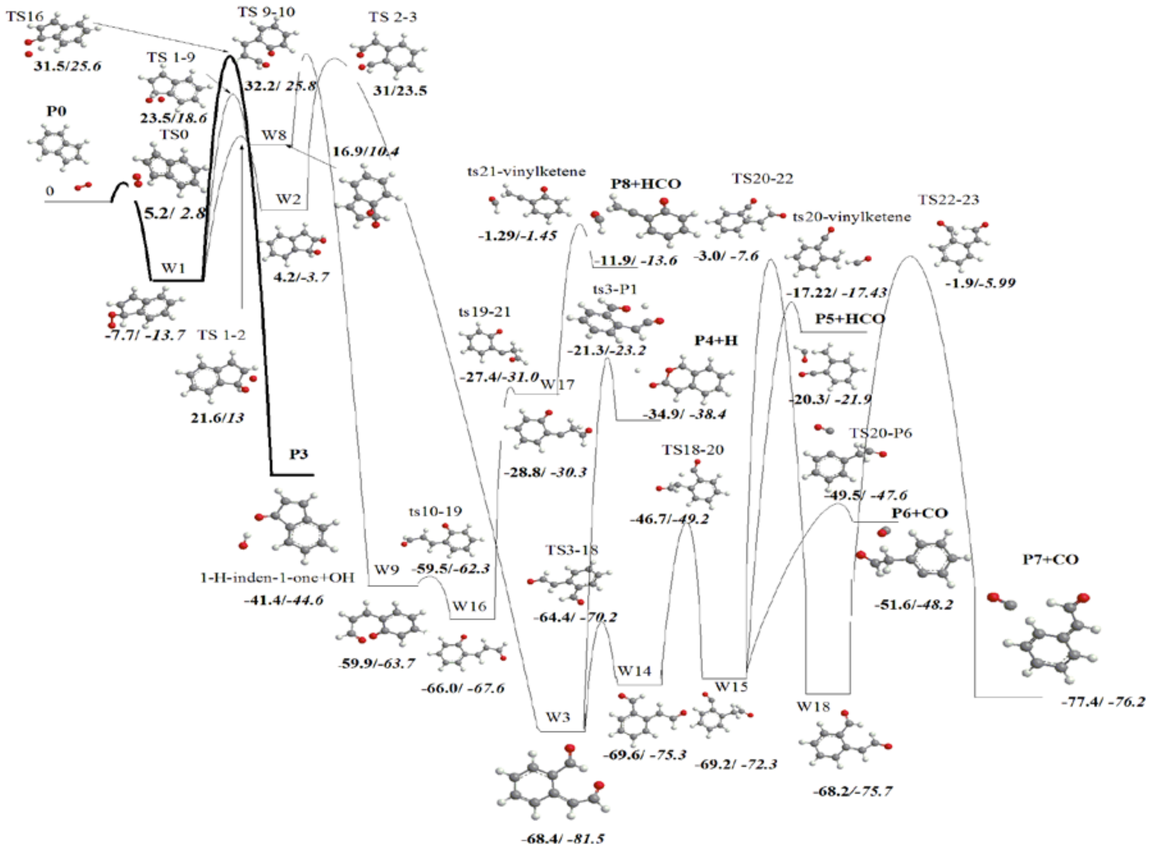


Figure 1. Potential energy diagram for the entrance channel of the $C_5H_5 + O_2$ reaction and pathways leading to the formation of cyclopentadienone C_5H_4O + OH (P1), C_5H_5O + O (P2), and the OC(H)CHCHCHC(H)O intermediate W3. All relative energies calculated at the CCSD(T)-F12/cc-pVTZ-f12//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) level of theory are given in kcal/mol with respect to the $C_5H_5 + O_2$ reactants.

Reaction product	1125 K	1375 K	1500 K	1800 K	2000 K
Pressure = 0.03, 1, 10, 100 atm					
Cyclopentadienone	$7.84 \cdot 10^{-18}$	$9.47 \cdot 10^{-17}$	$2.5 \cdot 10^{-16}$	$1.59 \cdot 10^{-15}$	$4.17 \cdot 10^{-15}$

The reaction of C_9H_7+O_2

The main reaction channels for the indenyl C_9H_7 oxidation – two-step pathway of 1-H-inden-1one formation, accompanied by OH elimination. The another probable way includes the isomerization of W1 to W2 and the ring opening, further the cis-trans isomerization occurs in W14, the hydrogen atom transfer from HCO side of the chain to CHCHO side (W15) and the CO detachment (P5+CO). Also probable outcome of coumarin can occur in the course of reaction chain $C_9H_7+O_2 \rightarrow TS0 \rightarrow W1 \rightarrow TS1\text{-}9 \rightarrow W8 \rightarrow TS9\text{-}10 \rightarrow W9 \rightarrow TS10\text{-}11 \rightarrow W10 \rightarrow TS10\text{-}P11 \rightarrow$ coumarin+H.

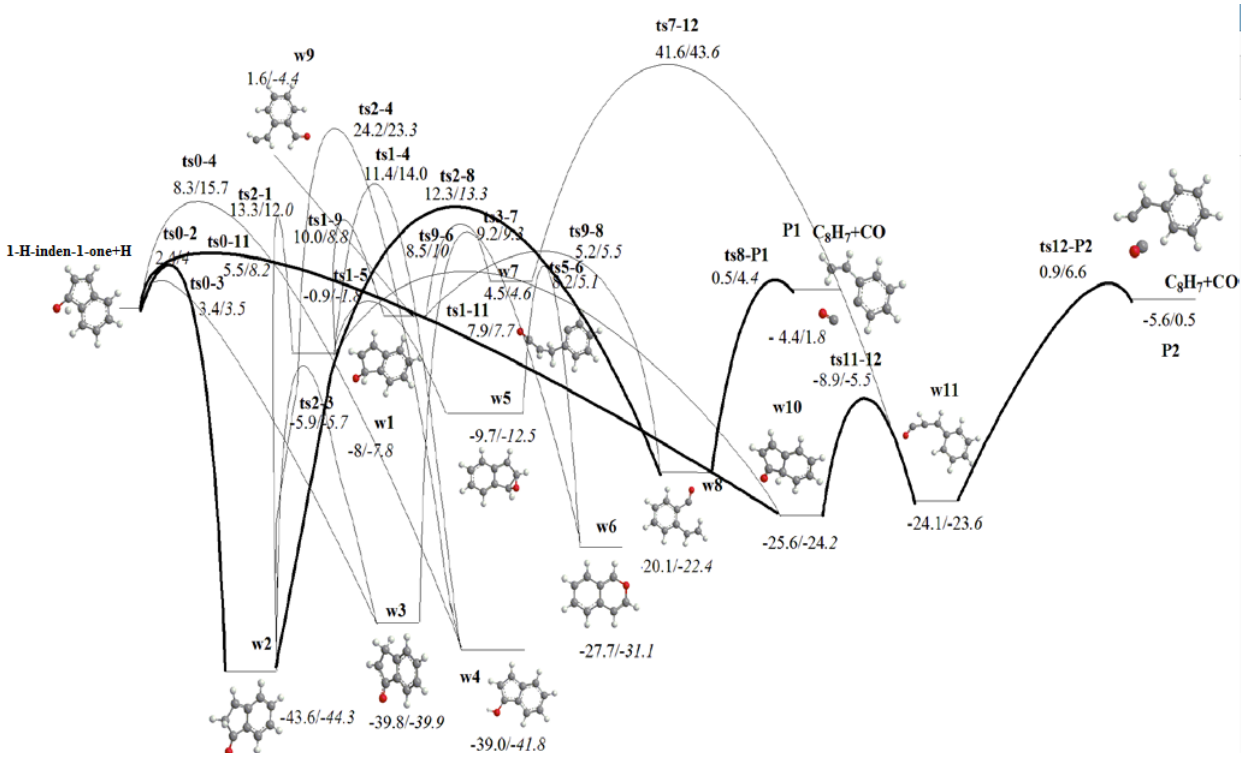


The branching coefficients for the described reaction pathways are shown in the table

T, K	1-H-inden-1-one (P3) + OH	P5 + CO	coumarin (P11) + H
1000	65.78%	26.66%	7.44%
1125	67.97%	24.17%	7.69%
1250	69.83%	22.14%	7.81%
1375	71.43%	20.44%	7.84%
1500	72.81%	18.99%	7.80%
1650	74.26%	17.52%	7.67%
1800	75.52%	16.25%	7.49%
2000	76.95%	14.81%	7.16%
2250	78.45%	13.29%	6.63%
2500	79.70%	11.99%	5.97%

The reaction of 1-H-inden-1-one + H

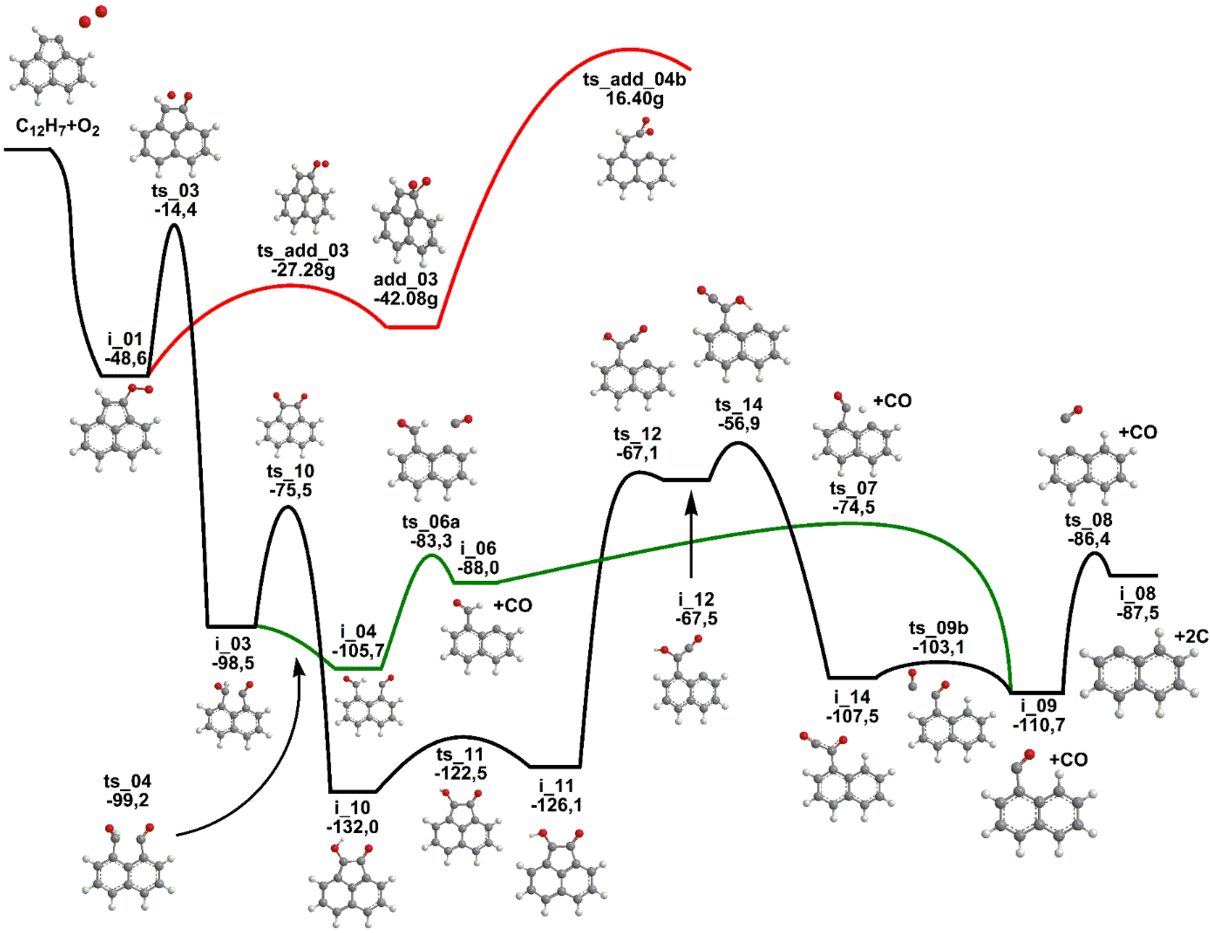
The most probable product of the reaction described above is 1-H-inden-1-one reacts with abundant in combustion flames H atom. The most probable two reaction pathways: the styrenyl formation P2 - P0→TS0-11→W10→TS11-12→W11→TS12-P2→P2 and ortho-vinyl phenyl formation pathway P1 - P0→TS0-2→W2→TS2-8→W8→TS8-P1→P1.



Reaction	$k_{0.1\ atm}$	$k_{1\ atm}$	$k_{10\ atm}$	$k_{100\ atm}$
1-H- inden-1-one+ H → C_8H_7 + CO (P1)				
1250 K	1.64×10^{-12}	1.23×10^{-11}	6.17×10^{-13}	1.79×10^{-13}
1500 K	5.27×10^{-12}	4.94×10^{-12}	3.88×10^{-12}	2.08×10^{-12}
1650 K	8.61×10^{-12}	8.61×10^{-12}	7.66×10^{-12}	5.27×10^{-12}
1800K	1.36×10^{-11}	1.36×10^{-11}	1.27×10^{-11}	1.03×10^{-11}
2000 K	2.22×10^{-11}	2.21×10^{-11}	2.21×10^{-11}	1.97×10^{-11}
2250 K	3.68×10^{-11}	3.68×10^{-11}	3.67×10^{-11}	3.66×10^{-11}
2500 K	5.61×10^{-11}	5.61×10^{-11}	5.61×10^{-11}	5.59×10^{-11}
1-H- inden-1-one+ H → C_8H_7 + CO (P2)				
1250 K	1.04×10^{-12}	1.03×10^{-12}	1.03×10^{-12}	1.03×10^{-12}
1500 K	2.17×10^{-12}	2.16×10^{-12}	2.14×10^{-12}	2.13×10^{-12}
1650 K	3.05×10^{-12}	3.05×10^{-12}	3.03×10^{-12}	3.01×10^{-12}
1800K	4.08×10^{-12}	4.08×10^{-12}	4.07×10^{-12}	4.03×10^{-12}
2000 K	5.65×10^{-12}	5.64×10^{-12}	5.63×10^{-12}	5.59×10^{-12}
2250 K	7.84×10^{-12}	7.84×10^{-12}	7.83×10^{-12}	7.80×10^{-12}
2500 K	1.02×10^{-11}	1.02×10^{-11}	1.02×10^{-11}	1.02×10^{-11}

The contribution of ortho-vinyl phenyl C_8H_7 (P1) and styrenyl C_8H_7 (P2) become significant with rising of temperature from 1500 K to 2500 K. The lowering of pressure does not influence on the rate constants dependence on temperature. The rising of pressure from 0.1 atm to 100 atm changes the products distribution in the range of T=1800..2500 K. At 0.1…1 atm the main reaction channels lead to P1 and P2, with rising pressure to 100 atm the distribution is between P1, P2 and W4, its formation becomes significant only at high temperatures and pressures. The most probable way, leading to W4, includes only one step P0→TS0-4→W4. It is initiated by H attachment to atom O position, out of the ring.

Oxidation of 1-acenaphthyl with molecular oxygen



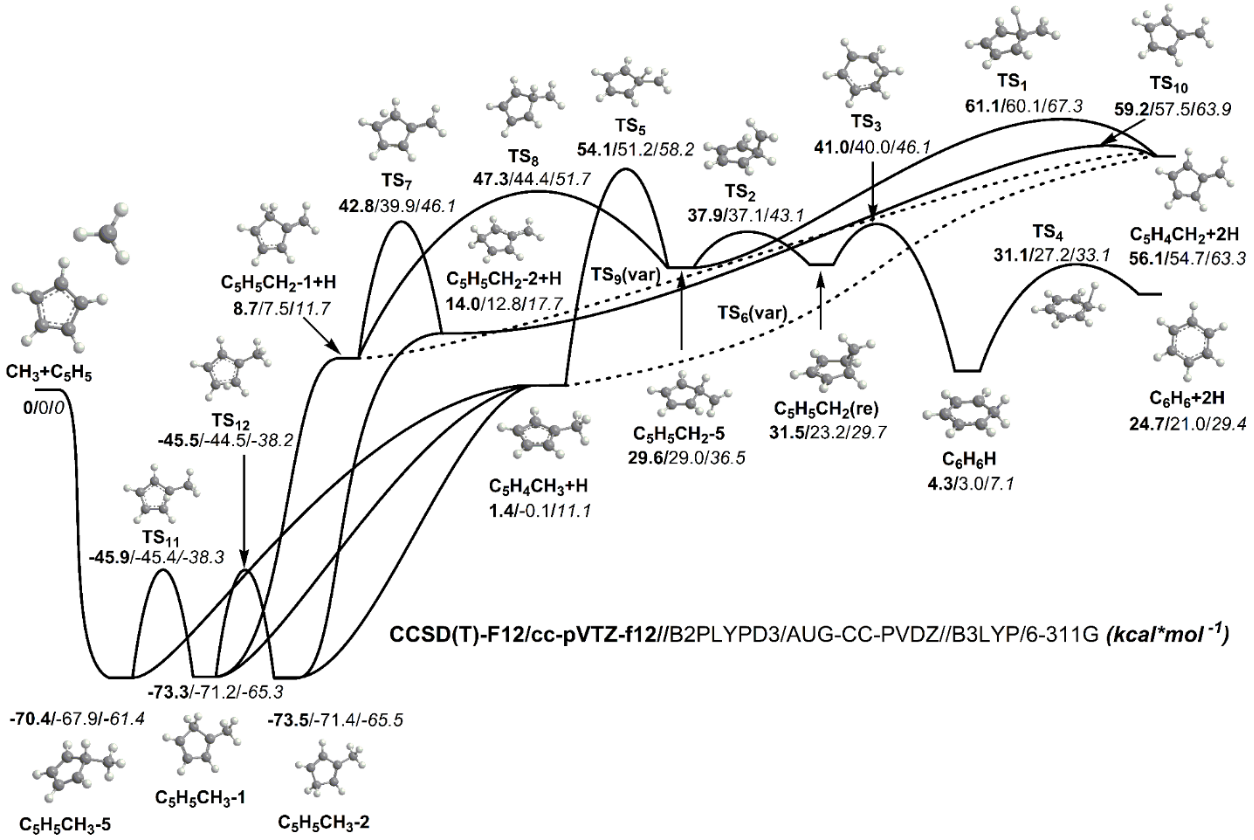
Schematic profile of the potential energy surface for the 1-acenaphthyl + $O_2(\,^3\Sigma_g^-)$ reaction. Index “g” stands for values obtained at B3LYP/6-311++G** level.

the most preferable path of the reaction 1-acenaphthyl + $O_2(\,^3\Sigma_g^-)$ leads eventually to formation of 1-naphthyl and consists of two subsequent CO-eliminations. The second one is much faster than the first, which turns out to be rate determining. Another crucial step is the entrance channel – initial formation of the 1 - acenaphthyl peroxy radical. This elementary reaction was treated in two different ways: using variable reaction coordinate transition-state theory (VRC-TST) or phase space theory. Both obtained in such ways sets of temperature and pressure dependencies demonstrate rather alike qualitative behavior, with high-pressure values tending to converge at highest temperatures. The ultimate quest of calculation of the total rate constant for reaction 1-acenaphthyl + $O_2(\,^3\Sigma_g^-)$ → 1 - naphthyl + 2 CO fails because of strong dependency on initial reagents concentrations. Thus, the reaction, in general, should be considered in steps: initial addition 1-acenaphthyl + $O_2({}^3\Sigma_g^-)$ → 1 - acenaphthyl peroxy radical and monomolecular dissociation 1 - acenaphthyl peroxy radical → 1 - naphthyl + 2 CO.

Pressure, atm	Arrhenius approximation
1-acenaphthyl + $O_2({}^3\Sigma_g^-) \rightarrow$ 1 - acenaphthyl peroxy radical	
0.01	0.43935E+80*6.02E+23*T^(-28.032) exp(-18431/T)+ 0.56655E+52*6.02E+23*T^(-20.518) exp(-8854.9/T)
0.1	0.61047E+81*6.02E+23*T^(-27.676) exp(-22084/T)+ 0.59128E+44*6.02E+23*T^(-17.516) exp(-8902.2/T)
1	0.11099E+63*6.02E+23*T^(-21.668) exp(-19671/T)+ 0.90767E+32*6.02E+23*T^(-13.703) exp(-7144.1/T)
10	0.21208E+55*6.02E+23*T^(-18.976) exp(-20581/T)+ 0.33411E+12*6.02E+23*T^(-7.1799) exp(-3893.2/T)
100	0.50672E+36*6.02E+23*T^(-13.326) exp(-17188/T)+ 135.51*6.02E+23*T^(-4.2149) exp(-2296.5/T)
1-acenaphthyl + $O_2({}^3\Sigma_g^-) \rightarrow$ i_06 (P1)	
0.01	0.17489E+32*6.02E+23*T^(-12.563) exp(-11839/T)+ 0.33023E-01*6.02E+23*T^(-2.8046) exp(-5231.4/T)
0.1	0.39990E+24*6.02E+23*T^(-10.034) exp(-11890/T)+ 0.18934E+27*6.02E+23*T^(-9.9509) exp(-25782/T)
1	0.95756E+71*6.02E+23*T^(-23.434) exp(-29966/T)+ 0.17489E+08*6.02E+23*T^(-5.1369) exp(-9869.6/T)
10	0.28417E+42*6.02E+23*T^(-14.563) exp(-24665/T)+ 0.33482E-10*6.02E+23*T^(-0.20672) exp(-5440.1/T)
100	0.20502E+24*6.02E+23*T^(-9.2520) exp(-21789/T)+ 0.76945E-12*6.02E+23*T^(-0.73738E-01) exp(-5676.7/T)
1 - acenaphthyl peroxy radical → 1-acenaphthyl + $O_2({}^3\Sigma_g^-)$	
0.01	0.69367E+96*T^(-25.039) exp(-39082/T)+ 0.38004E+76*T^(-20.562) exp(-29635/T)
0.1	0.91527+101*T^(-25.904) exp(-43584/T)+ 0.17615E+72*T^(-17.830) exp(-32811/T)
1	0.27971+100*T^(-24.968) exp(-46106/T)+ 0.15136E+49*T^(-10.377) exp(-29397/T)
10	0.10184E+79*T^(-18.328) exp(-42454/T)+ 0.31298E+42*T^(-8.2353) exp(-28359/T)
100	0.19302E+62*T^(-13.258) exp(-39342/T)+ 0.24758E+35*T^(-5.9823) exp(-27186/T)
1 - acenaphthyl peroxy radical → i_06 (P1)	
0.01	0.12815E+71*T^(-17.602) exp(-28678/T)+ 0.11246E+58*T^(-15.175) exp(-21375/T)
0.1	0.18836E+73*T^(-24.418) exp(-9767.4/T)+ 0.75015+122*T^(-32.525) exp(-42961/T)
1	0.49927+145*T^(-38.363) exp(-56754/T)+ 0.78715E+29*T^(-4.9867) exp(-20175/T)
10	0.21017E+50*T^(-10.541) exp(-28472/T)+ 0.42752E+33*T^(-6.2835) exp(-20447/T)
100	0.17076E+49*T^(-9.9858) exp(-30652/T)+ 0.44209E+23*T^(-3.0319) exp(-19060/T)

Five-membered rings growth

Reverse process of five-membered rings growth was studied using model reactions of methyl with analogous species: cyclopentadienyl and molecules, in which five-membered ring was embedded into a group of six-membered rings. For C_5H_5+CH_3 reaction, it was shown, that five-membered ring can be effectively transformed into six-membered one.

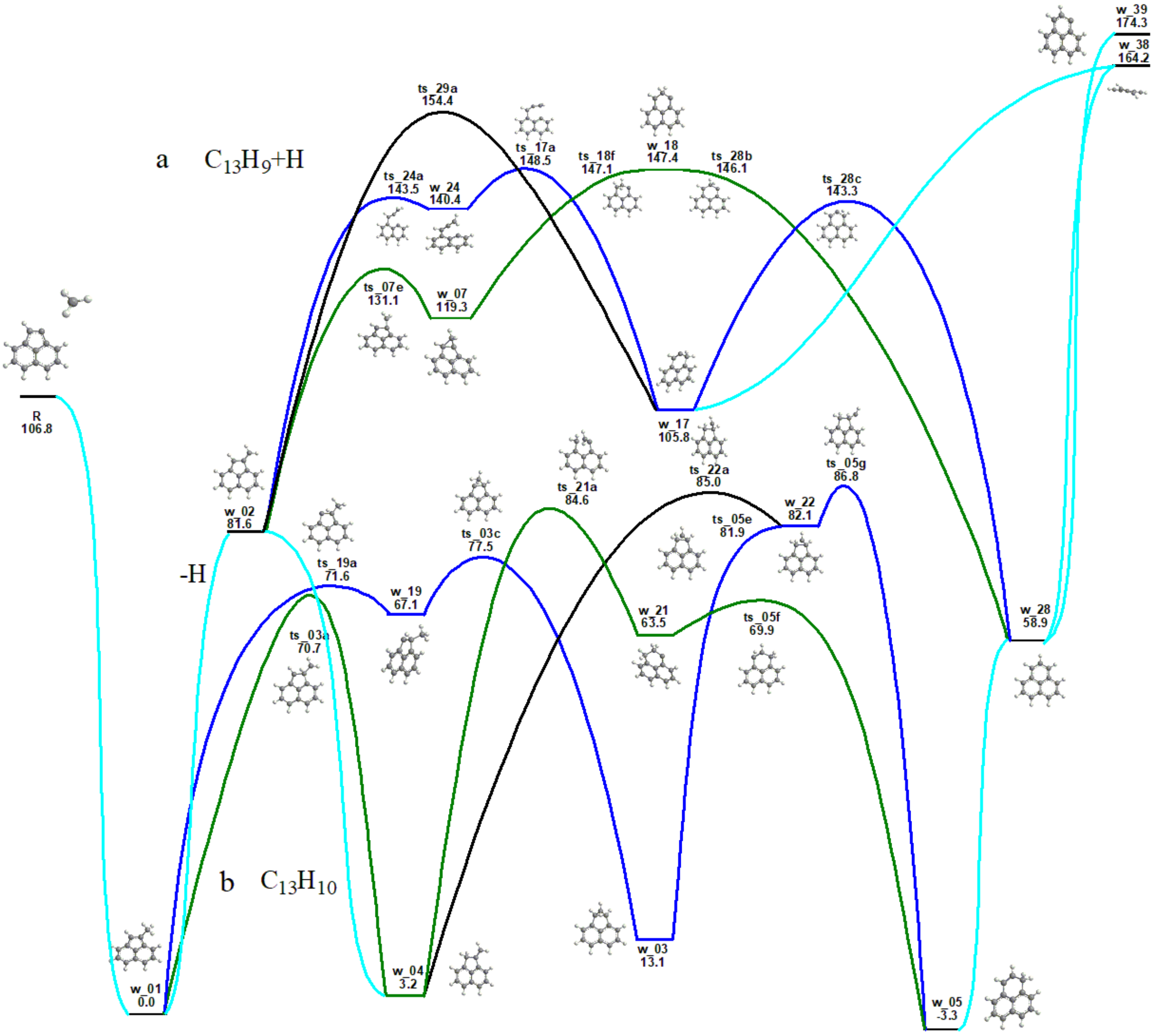


Reaction pathways involved in transformations of C_5 and C_6 ring species. Blue and red arrows depict processes that result in $C_6 \rightarrow C_5$ and $C_6 \leftarrow C_5$ transformations, respectively, whereas black arrows show processes that do not lead to a change in the number of C atoms in the ring.

product	temperatures (K)				
	1100	1300	1500	1700	2000
			p = 0.01 atm		
fulvene	$1.23{\cdot}10^{-12}$	$1.87{\cdot}10^{-12}$	$2.57{\cdot}10^{-12}$	$3.29{\cdot}10^{-12}$	$4.24{\cdot}10^{-12}$
benzene	$3.40{\cdot}10^{-12}$	$4.19{\cdot}10^{-12}$	$5.00{\cdot}10^{-12}$	$5.76{\cdot}10^{-12}$	$6.71{\cdot}10^{-12}$
			p = 1 atm		
fulvene	$1.39{\cdot}10^{-12}$	$2.32{\cdot}10^{-12}$	$3.51{\cdot}10^{-12}$	$4.77{\cdot}10^{-12}$	$6.34{\cdot}10^{-12}$
benzene	$3.25{\cdot}10^{-12}$	$3.75{\cdot}10^{-12}$	$4.07{\cdot}10^{-12}$	$4.28{\cdot}10^{-12}$	$4.60{\cdot}10^{-12}$
			p = 10 atm		
fulvene	$1.80{\cdot}10^{-12}$	$2.43{\cdot}10^{-12}$	$3.60{\cdot}10^{-12}$	$5.09{\cdot}10^{-12}$	$6.83{\cdot}10^{-12}$
benzene	$2.88{\cdot}10^{-12}$	$3.66{\cdot}10^{-12}$	$4.00{\cdot}10^{-12}$	$3.99{\cdot}10^{-12}$	$4.14{\cdot}10^{-12}$
			p = 100 atm		
fulvene	$2.83{\cdot}10^{-12}$	$4.45{\cdot}10^{-12}$	$6.24{\cdot}10^{-12}$	$5.90{\cdot}10^{-12}$	$7.71{\cdot}10^{-12}$

benzene	$1.39 \cdot 10^{-12}$	$1.53 \cdot 10^{-12}$	$1.44 \cdot 10^{-12}$	$3.27 \cdot 10^{-12}$	$3.36 \cdot 10^{-12}$

It was obtained, that five-membered ring can be transformed into six-membered one in reaction of methyl and 1-acenaphthyl in two ways with two products: phenalene and phenalenyl. Similarly to oxidation of acenaphthyl, it has no physical meaning to compute total reaction rate constant and one have to model process step by step.



Pyrolis of bromonaphthalene

Reaction rates constants for the C10H7Br dissociation were calculated using variable reaction coordinate transition state theory VRC-TST with help of ROTD and MESS software. Obtained values were used to develop new approach to analysis of processes inside high-temperature microreactors – one of the promising apparatuses for experimental measurement of kinetic data at temperatures below 2000 K.

Pressure, atm	Arrhenius approximation
1-bromonaphthalene -> 1-naphthyl + Br	
0.01	0.18499E+72*6.02E+23*T^(-15.996) exp(-62039/T)+ 0.10628E+37*6.02E+23*T^(-6.3626) exp(-46774/T)
0.0395	0.16205E+49*6.02E+23*T^(-9.4625) exp(-54064/T)+ 0.14640E+33*6.02E+23*T^(-5.1952) exp(-45949/T)

0.1	0.15415E+41*6.02E+23*T^(-7.2012) exp(-51148/T)+ 0.33574E+31*6.02E+23*T^(-4.7074) exp(-45579/T)
0.3	0.36434E+37*6.02E+23*T^(-6.1939) exp(-49774/T)+ 0.63690E+29*6.02E+23*T^(-4.1823) exp(-45233/T)
1	0.22209E+36*6.02E+23*T^(-5.8609) exp(-49291/T)+ 0.10727E+29*6.02E+23*T^(-3.9455) exp(-45081/T)
1-naphthyl + Br -> 1-bromonaphthalene	
0.01	0.67803E+42*6.02E+23*T^(-14.865) exp(-18301/T)+ 0.79684E+06*6.02E+23*T^(-5.0371) exp(-2779.8/T)
0.0395	0.35354E+19*6.02E+23*T^(-8.2669) exp(-10253/T)+ 104.98*6.02E+23*T^(-3.8631) exp(-1952.7/T)
0.1	0.26839E+11*6.02E+23*T^(-5.9767) exp(-7308.1/T)+ 3.0020*6.02E+23*T^(-3.4048) exp(-1601.3/T)
0.3	0.30894E+06*6.02E+23*T^(-4.6127) exp(-5308.6/T)+ 0.10636E-01*6.02E+23*T^(-2.6674) exp(-1080.6/T)
1	0.30347E+06*6.02E+23*T^(-4.6066) exp(-5417.4/T)+ 0.97895E-02*6.02E+23*T^(-2.6450) exp(-1106.4/T)
2- bromonaphthalene -> 2- naphthyl + Br	
0.01	0.16069E+69*6.02E+23*T^(-15.146) exp(-60998/T)+ 0.21865E+36*6.02E+23*T^(-6.1759) exp(-46601/T)
0.0395	0.24720E+47*6.02E+23*T^(-8.9683) exp(-53409/T)+ 0.54524E+32*6.02E+23*T^(-5.0892) exp(-45823/T)
0.1	0.16441E+39*6.02E+23*T^(-6.6761) exp(-50317/T)+ 0.31366E+30*6.02E+23*T^(-4.4242) exp(-45314/T)
0.3	0.18208E+37*6.02E+23*T^(-6.1291) exp(-49656/T)+ 0.31148E+29*6.02E+23*T^(-4.1107) exp(-45136/T)
1	0.11691E+36*6.02E+23*T^(-5.8021) exp(-49172/T)+ 0.61928E+28*6.02E+23*T^(-3.8971) exp(-44996/T)
2- naphthyl + Br -> 2- bromonaphthalene	
0.01	0.71442E+39*6.02E+23*T^(-14.020) exp(-17308/T)+ 0.21151E+06*6.02E+23*T^(-4.8629) exp(-2665.5/T)
0.0395	0.63068E+17*6.02E+23*T^(-7.7736) exp(-9638.8/T)+ 51.737*6.02E+23*T^(-3.7731) exp(-1887.4/T)
0.1	0.47123E+10*6.02E+23*T^(-5.7666) exp(-7042.3/T)+ 1.3318*6.02E+23*T^(-3.2984) exp(-1534.9/T)
0.3	0.13283E+06*6.02E+23*T^(-4.5124) exp(-5168.4/T)+ 0.64917E-02*6.02E+23*T^(-2.6045) exp(-1039.5/T)
1	4949.8*6.02E+23*T^(-4.1195) exp(-4545/T)+ 0.94566E-03*6.02E+23*T^(-2.3570) exp(-854.31/T)