Kinetic and reactivity of gas-phase reaction of acyclic dienes with hydroxyl radical in the 273-318 K temperature range

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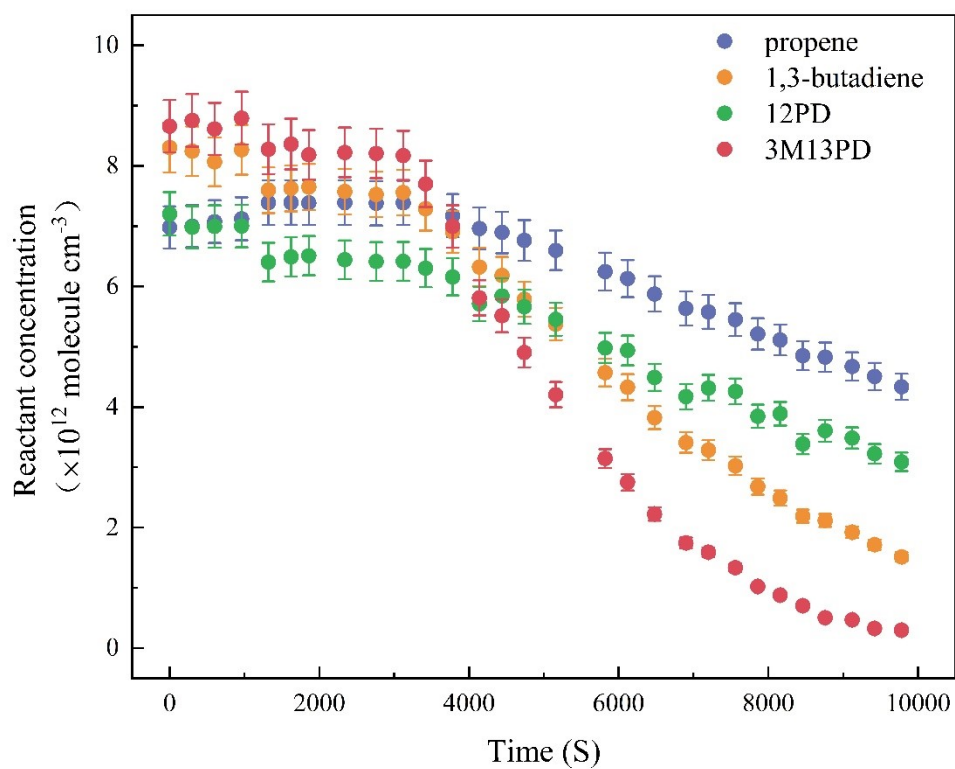
Fig S1. Example of plots of reactant consumption versus reaction time in the case of photolysis of hydrogen peroxide, the error bar was estimated from the uncertainty of GC-PID as 5%.
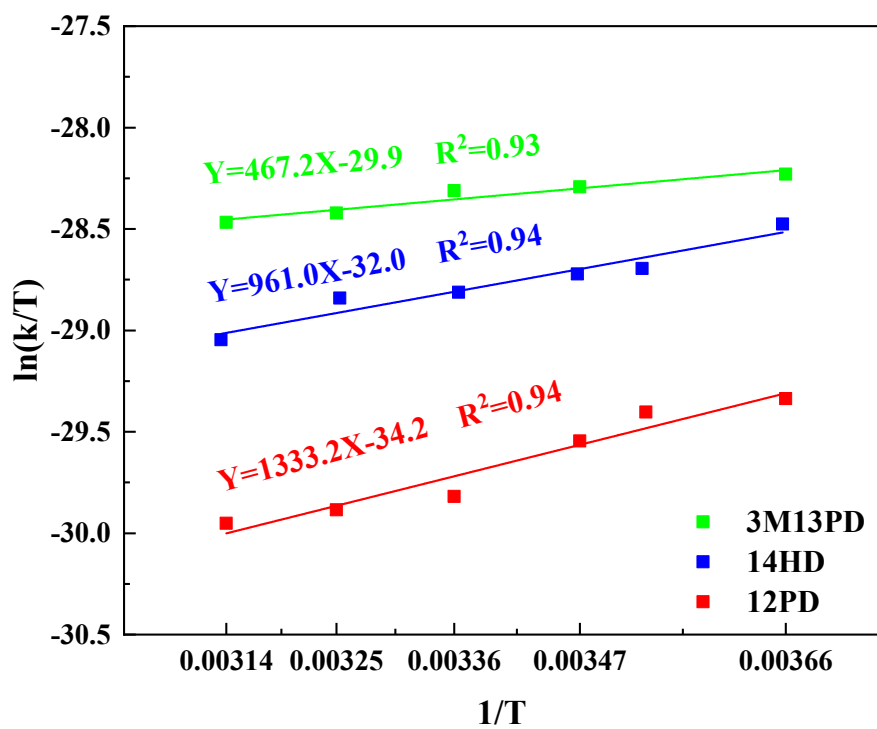
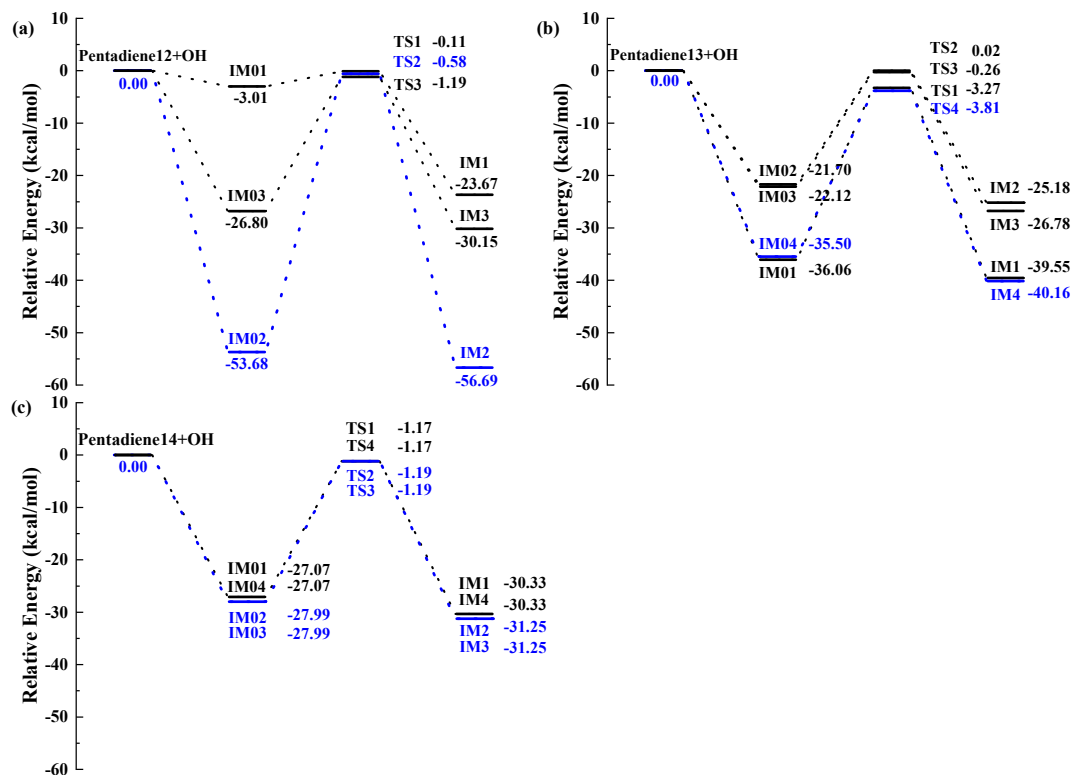**Fig S2.** Eyring plots showing temperature dependence behavior of the reaction of 3M13PD, 14HD and 12PD with ·OH.

Fig S3. Plot of Potential energy surface (PES) for the addition reaction of 1,2-pentadiene (a), 1,3-pentadiene (b) and 1,4-pentadiene (c) with ·OH. The blue scheme represents the minimum energy path.

Table S1. Experimental conditions and reaction rate coefficients for 3M-1,3-PD, 1,4-HD and 1,2-PD with OH radicals at temperatures of 273-318 K.

Diene	T(K)	Reference	$\dfrac{k_{diene}}{k_{ref}}$ [a]	k_{diene_ref} [b] 10^{-11} cm^3 molecule^{-1} s^{-1}	k_{av} [c] 10^{-11} cm^3 molecule^{-1} s^{-1}
3M-1,3-PD	273	propene	4.77±0.36	14.66±3.14	15.01±1.25
		1,3-butadiene	2.01±0.08	15.35±3.13	
	288	propene	5.87±0.06	14.50±3.11	14.86±1.22
		1,3-butadiene	1.96±0.01	14.34±3.17	
	308	propene	6.33±0.06	15.77±3.16	13.96±1.19
		1,3-butadiene	2.01±0.02	12.77±2.56	
	318	propene	6.32±0.03	14.94±3.00	13.78±1.18
		1,3-butadiene	2.13±0.01	12.92±2.58	
1,4-HD	273	propene	4.09±0.04	12.58±2.52	11.74±1.09
		1,3-butadiene	1.45±0.02	11.09±2.22	
	283	propene	3.48±0.04	10.02±2.01	9.78±0.99
		1,3-butadiene	1.33±0.01	9.56±1.92	
	288	propene	3.70±0.06	10.31±2.07	9.67±0.99
		1,3-butadiene	1.31±0.01	9.17±1.84	
	308	propene	4.22±0.04	10.52±2.11	9.17±0.96
		1,3-butadiene	1.31±0.01	8.32±1.67	
	318	propene	3.55±0.03	8.40±1.68	7.73±0.88
		1,3-butadiene	1.20±0.01	7.24±1.45	
1,2-PD	273	propene	1.74±0.12	5.33±1.13	4.96±0.73
		1,3-butadiene	0.61±0.05	4.67±1.00	
	283	propene	1.72±0.03	4.94±1.00	4.81±0.70
		1,3-butadiene	0.65±0.01	4.69±0.94	
	288	propene	1.63±0.08	4.55±0.93	4.24±0.66
		1,3-butadiene	0.57±0.03	4.00±0.84	
	308	propene	1.47±0.02	3.65±0.73	3.23±0.57
		1,3-butadiene	0.47±0.01	2.96±0.59	
	318	propene	1.42±0.02	3.56±0.71	3.12±0.56
		1,3-butadiene	0.49±0.01	3.06±0.62	

[a] k_{ref} extracted from Calvert, Jack G. et al. "The Mechanisms of Atmospheric Oxidation of the Alkenes." (2000)[1].

$$\sigma_k = \frac{k}{k_{ref}} k_{ref} \sqrt{\left(\frac{\sigma_{ref}}{k_{ref}}\right)^2 + \left(\frac{\sigma_{k/k_{ref}}}{\frac{k}{k_{ref}}}\right)^2}$$

[b] The error was calculated as follows:

[c] Weighted average[3] $k_{av}= (w_{diene\_ref1}k_{diene\_ref1}+w_{diene\_ref2}k_{diene\_ref2} + \ldots)/ (w_{diene\_ref1}+w_{diene\_ref2}+ \ldots)$, where $w_{diene\_ref1} = 1/\sigma_{diene\_ref1}^2$, etc. The error, σ_{av}, was given by: $\sigma_{av}= (1/\sigma_{diene\_ref1}+1/\sigma_{diene\_ref2}+\ldots)^{-0.5}$.

Table S2. Summary of activation parameters obtained with the Arrhenius and Eyring equations

Diene	T range (K)	Arrhenius parameters		Eyring parameters	
		E_a (kJ mol^{-1})	ln A	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1}mol^{-1})
3M13PD	273-318	-1.44	-23.24	-3.91	-446.39
14HD	273-318	-5.54	-25.35	-7.99	-463.88
12PD	273-318	-8.63	-27.51	-11.09	-481.84

Table S3. The rate constants for the reaction of OH radicals with dienes and corresponding mono-alkenes are summarized based on a database at 298K and 1 atm and their structural formulae. The new SAR calculated values are listed at the end.

Diene	Structure	k_{exp}[a] 10^{-11} cm^3 molecule^{-1} s^{-1}	Mono-alkene	Structure	k_{exp}[a] 10^{-11} cm^3 molecule^{-1} s^{-1}	k_{cal}[c] 10^{-11} cm^3 molecule^{-1} s^{-1}	k_{pred} 10^{-11} cm^3 molecule^{-1} s^{-1}
1,3-butadiene	C=CC=C	6.63±1.00	1-butene	C=CCC	3.10±0.63	6.20	6.97[d]
			1-butene	C=CCC	3.10±0.63		
isoprene	C=C(C)C=C	10.00±1.48	3-methyl-1-butene	C=CC(C)C	3.18±0.64	9.28	10.43[d]
			2-methyl-1-butene	C=C(C)CC	6.10±1.83		
(Z)-1,3-pentadiene	C/C=C\C=C	10.70±2.68	1-pentene	C=CCCC	3.22±0.48	9.72	10.92[d]
			2-pentene	CC=CCC	6.50±2.00		
(3E)-penta-1,3-diene	C/C=C/C=C	11.60±4.35	1-pentene	C=CCCC	3.22±0.48	9.72	10.92[d]
			2-pentene	CC=CCC	6.50±2.00		
2-methyl-1,3-pentadiene	CC=CC(=C)C	13.60±4.10	2-methyl-1-pentene	C=C(C)CCC	6.14±1.23	12.24	13.75[d]
			4-methyl-2-pentene	CC=CC(C)C	6.10±1.83		
(3E)-hexa-1,3-diene	CC/C=C/C=C	11.20±3.40	1-hexene	C=CCCCC	3.70±1.11	9.97	11.20[d]
			3-hexene	CCC=CCC	6.27±0.66		
(Z/E)-2,4-hexadiene	CC=CC=CC	13.40±4.02	2-hexene	CC=CCCC	6.08±1.22	12.16	13.66[d]
			2-hexene	CC=CCCC	6.08±1.22		
1,4-pentadiene	C=CCC=C	5.41±1.08	1-pentene	C=CCCC	3.22±0.48	6.45	5.81[e]
			1-pentene	C=CCCC	3.22±0.48		
(E)-1,4-hexadiene	C=CC/C=C/C	9.10±2.73	1-hexene	C=CCCCC	3.70±1.11	9.78	8.81[e]
			2-hexene	CC=CCCC	6.08±1.22		
1,5-hexadiene	C=CCCC=C	6.20±1.24	1-hexene	C=CCCCC	3.70±1.11	7.4	6.67[e]
			1-hexene	C=CCCCC	3.70±1.11		

(Z/E)-1,4-hexadiene [b]	C=CCC=CC	9.13±0.62	1-hexene	C=CCCC	3.70±1.11	9.78	8.81[e]
			2-hexene	CC=CCCC	6.08±1.22		

[a] k_{exp} extracted from M. R. McGillen. et al. "Database for the kinetics of the gas-phase atmospheric reactions of organic compounds. " (2020)[4].

[b] Rate constants from this work.

[c] The rate coefficients of conjugated diene and isolated diene reaction wih OH radical by summing up the rate coefficients of corresponding mono-alkene that we derived by converting one C=C bond to a C-C bond, e.g.,1,4-hexadiene→ 1-hexene + 2-hexene. In this way, $k_{cal\_1,4\text{-hexadiene}}=k_{1\text{-hexene}}+k_{2\text{-hexene}}$.

[d] and [e] The k_{pred} is obtained by multiplying k_{cal} by the factors of 0.89 and 1.11, respectively, derived from Fig 5. for conjugated and isolated dienes.

Table S4. The number of carbon atoms and the rate coefficients for the reaction with OH of a series of straight-chain dienes including cumulated diene (C=C=C), conjugated diene (C=C-C=C), and isolated diene (C=C-(C)$_n$-C=C, n$\geqslant$1).

Diene	Number of carbon atoms	Rate coefficients (cm^3 molecule^{-1} s^{-1})[a] 10^{-11} cm^3 molecule^{-1} s^{-1}
C=C=C		
Propadiene	3	0.98±0.20
1,2-butadiene	4	2.60±0.80
1,2-pentadiene	5	3.60±1.10
C=C-C=C		
1,3-butadiene	4	6.63±1.00
(Z)-1,3-pentadiene	5	10.70±2.68
(3E)-penta-1,3-diene	5	11.60±4.35
(3E)-hexa-1,3-diene	6	11.20±3.40
(Z/E)-2,4-hexadiene	6	13.40±4.02
C=C-(C)$_n$-C=C		
1,4-pentadiene	5	5.41±1.08
(E)-1,4-hexadiene	6	9.10±2.73
1,5-hexadiene	6	6.20±1.24

[a] The rate coefficients of dienes reacting with the OH extracted from M. R. McGillen. et al. "Database for the kinetics of the gas-phase atmospheric reactions of organic compounds. " (2020)[4]

Table S5. The relationship of rate coefficients of dienes reaction with OH radical vs the number of alkyl groups on the diene.

Diene	Structure	k_{exp} [a] 10^{-11} cm^3 molecule^{-1} s^{-1}	alkyl groups on the base structures [c]
C=C=C			
Propadiene	C=C=C	0.98±0.20	**C=C=C**
1,2-butadiene	C=C=CC	2.60±0.80	-CH$_3$
3-methyl-1,2-butadiene	C=C=C(C)C	5.70±1.71	2*-CH$_3$
1,2-pentadiene	CCC=C=C	3.34±0.40 [b]	-CH$_2$CH$_3$
C=C-C=C			
1,3-butadiene	C=CC=C	6.63±1.00	**C=C-C=C**
isoprene	C=C(C)C=C	10.00±1.48	-CH$_3$
(Z)-1,3-pentadiene	C/C=C\C=C	10.70±2.68	-CH$_3$
(3E)-penta-1,3-diene	C/C=C/C=C	11.60±4.35	-CH$_3$
4-methyl-1,3-pentadiene	C=CC=C(C)C	13.10±3.93	2*-CH$_3$
2,3-dimethyl-1,3-butadiene	CC(=C)C(=C)C	12.20±3.70	2*-CH$_3$
2-methyl-1,3-pentadiene	CC=CC(=C)C	13.60±4.10	2*-CH$_3$
(3E)-hexa-1,3-diene	CC/C=C/C=C	11.20±3.40	-CH$_2$CH$_3$
(Z/E)-2,4-hexadiene	CC=CC=CC	13.40±4.02	2*-CH$_3$
3-methyl-1,3-pentadiene	C=CC(C)=CC	15.09±0.72 [b]	2*-CH$_3$
2,5-dimethyl-2,4-hexadiene	CC(=CC=C(C)C)C	2.10±0.63	4*-CH$_3$
C=C-(C)$_n$-C=C			
1,4-pentadiene	C=CCC=C	5.41±1.08	**C=C-C-C=C**
2-methyl-1,4-pentadiene	C=CCC(=C)C	7.90±2.40	-CH$_3$
(E)-1,4-hexadiene	C=CC/C=C/C	9.10±2.73	-CH$_3$
1,5-hexadiene	C=CCCC=C	6.20±1.24	**C=C-C-C-C=C**

(Z/E)-1,4-hexadiene	C=CCC=CC	9.13±0.62 [b]	-CH$_3$
2,5-dimethyl-1,5-hexadiene	CC(=C)CCC(=C)C	12.00±3.60	2*-CH$_3$

[a] k_{exp} extracted from M. R. McGillen. et al. "Database for the kinetics of the gas-phase atmospheric reactions of organic compounds. " (2020)[4].

[b] Rate constants from this work.