

## Crigeer 中间体 $\text{CH}_3\text{CHOO}$ 与 $\text{H}_2\text{O}$ 反应机理及酸催化效应

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## Reaction Mechanism of Crigeer Intermediate $\text{CH}_3\text{CHOO}$ with $\text{H}_2\text{O}$ and the Acid Catalytic Effect

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表 S1 CCSD(T)//B3LYP/6-311+G(*d,p*)水平上标题反应的相对能量、相对焓、相对吉布斯自由能(kJ mol<sup>-1</sup>)和  $T_1$  检验值

Table S1 Relative energies, relative enthalpies, relative Gibbs free energies (kJ mol<sup>-1</sup>), and

$T_1$  for the title reaction system at the CCSD(T)//B3LYP/6-311+G(*d,p*) level

	$pK_a$	stationary point	CH <sub>3</sub> CHOO	$\Delta E$	$\Delta H$	$\Delta G$	$T_1$
non-catalytic	-	RC	<i>syn</i> -	-29.14	-30.99	4.43	0.031
			<i>anti</i> -	-33.51	-35.47	-1.24	0.029
		TS	<i>syn</i> -	39.98	32.69	81.95	0.024
			<i>anti</i> -	10.36	3.04	51.26	0.023
		PC	<i>syn</i> -	-153.79	-159.22	-113.81	0.012
			<i>anti</i> -	-172.02	-177.89	-132.10	0.012
H <sub>2</sub> O	15.7	RC	<i>syn</i> -	-68.11	-72.22	-0.40	0.026
			<i>anti</i> -	-74.92	-79.63	-7.11	0.024
		TS	<i>syn</i> -	-27.33	-39.15	52.93	0.018
			<i>anti</i> -	-43.78	-56.13	36.54	0.018
		PC	<i>syn</i> -	-182.43	-191.05	-105.80	0.012
			<i>anti</i> -	-198.74	-208.06	-121.79	0.012
CH <sub>3</sub> CH <sub>2</sub> COOH	4.87	RC	<i>syn</i> -	-93.96	-94.48	-15.75	0.022
			<i>anti</i> -	-97.93	-99.90	-19.0	0.021
		TS	<i>syn</i> -	-73.41	-80.02	15.54	0.019
			<i>anti</i> -	-84.70	-91.59	2.79	0.019
		PC	<i>syn</i> -	-201.50	-206.92	-116.81	0.014
			<i>anti</i> -	-220.24	-226.21	-134.09	0.014
CH <sub>3</sub> COOH	4.75	RC	<i>syn</i> -	-93.87	-94.61	-15.88	0.023
			<i>anti</i> -	-99.95	-102.11	-19.10	0.015
		TS	<i>syn</i> -	-74.65	-81.41	13.52	0.019
			<i>anti</i> -	-86.22	-93.37	1.54	0.019
		PC	<i>syn</i> -	-204.42	-210.09	-118.23	0.015
			<i>anti</i> -	-219.59	-225.75	-133.36	0.015
HCOOH	3.75	RC	<i>syn</i> -	-95.03	-96.54	-17.64	0.024
			<i>anti</i> -	-101.85	-104.64	-22.25	0.023
		TS	<i>syn</i> -	-76.15	-83.40	10.66	0.020
			<i>anti</i> -	-89.23	-96.88	-2.09	0.020
		PC	<i>syn</i> -	-202.28	-208.53	-117.08	0.015
			<i>anti</i> -	-217.66	-224.40	-132.45	0.015
CH <sub>2</sub> ClCOOH	2.86	RC	<i>syn</i> -	-104.26	-104.82	-24.69	0.022
			<i>anti</i> -	-111.05	-112.91	-28.97	0.021
		TS	<i>syn</i> -	-88.02	-94.02	0.72	0.019
			<i>anti</i> -	-101.54	-107.87	-12.36	0.019

CH <sub>2</sub> FCOOH	2.59	PC	<i>syn</i> -	-207.31	-212.67	-121.14	0.014
			<i>anti</i> -	-222.63	-228.54	-136.28	0.014
		RC	<i>syn</i> -	-100.74	-101.41	-22.18	0.023
			<i>anti</i> -	-107.90	-109.95	-26.76	0.021
		TS	<i>syn</i> -	-85.71	-91.82	2.44	0.019
			<i>anti</i> -	-98.79	-105.11	-10.65	0.019
(COOH) <sub>2</sub>	1.23	PC	<i>syn</i> -	-208.25	-213.69	-121.51	0.015
			<i>anti</i> -	-223.51	-229.44	-136.70	0.015
		RC	<i>syn</i> -	-106.06	-106.32	-26.32	0.020
			<i>anti</i> -	-113.54	-115.34	-29.99	0.022
		TS	<i>syn</i> -	-95.45	-100.62	-6.16	0.020
			<i>anti</i> -	-109.02	-114.13	-20.85	0.020
PC	<i>syn</i> -	-207.41	-212.55	-119.21	0.016		
	<i>anti</i> -	-222.70	-228.35	-134.85	0.016		

表 S2 B3LYP/6-311+G(*d,p*)水平上 CH<sub>3</sub>CHOO+H<sub>2</sub>O 反应中转移 H 的电荷密度

Table S2 Electric density of transfer H in CH<sub>3</sub>CHOO+H<sub>2</sub>O reaction at the B3LYP/6-311+G(*d,p*) level

		Mulliken		NBO	
		H	OH	H	OH
non-catalytic	RC1-s	+0.311	-0.630	+0.484	-0.971
	RC2-a	+0.290	-0.586	+0.482	-0.973
	TS2-s	+0.331	-0.461	+0.484	-0.845
	TS2-a	+0.336	-0.489	+0.479	-0.860
	<i>syn</i> -HAHP	+0.260	-0.295	+0.465	-0.728
	<i>anti</i> -HAHP	+0.269	-0.306	+0.466	-0.738
H <sub>2</sub> O-catalytic	RC3-s	+0.379	-0.643	+0.500	-0.975
	RC3-a	+0.383	-0.630	+0.502	-0.978
	TS3-s	+0.467	-0.476	+0.507	-0.831
	TS3-a	+0.476	-0.490	+0.508	-0.831
	PC3-s	+0.319	-0.378	+0.490	-0.774
	PC3-a	+0.321	-0.381	+0.491	-0.770

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	RC4-s	+0.411	-0.667	+0.506	-0.973
	RC4-a	+0.420	-0.637	+0.509	-0.960
HCOOH-catalytic	TS4-s	+0.479	-0.524	+0.517	-0.870
	TS4-a	+0.462	-0.510	+0.519	-0.873
	PC4-s	+0.425	-0.427	+0.510	-0.778
	PC4-a	+0.429	-0.425	+0.511	-0.776

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