Supplementary Material

For

"A multiscale simulation on the formation mechanism of crotonaldehyde and the influence of operating parameters on the process during the production of vinyl acetate from acetylene"

By

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Table 1. Activation Energy of Each Elementary Event in the Process of Producing Vinyl Acetate from Acetylene on the Zinc Acetate (220) Surface

No.	Elementary reaction	$E_{a,f}$/eV	$E_{a,r}$/eV
1[a]	CHCH(g) + * ↔ CHCH*	0	0.98
2	CH_3COOH(g) + * ↔ CH_3COOH*	0	1.2
3	H_2O(g) + * ↔ H_2O*	0	1.03
4	CH_3COOH* ↔ CH_3COO* + H*	0.91	0.59
5	CHCH* + H* ↔ CH_2CH*	0.04	2.1
6	CH_3COO* + CH_2CH* ↔$CH_3COOCHCH_2$*	0.11	3.57
7	CH_3COOH* + CHCH* ↔$CH_3COOCHCH_2$*	0.4	3.67
8	CHCH* + CHCH* ↔ CHCHCHCH*	0.25	3.5
9	CHCH* ↔ CHC* + H*	0.59	0.35
10	CHCH* + CHC* ↔ CHCCHCH*	0.57	2.53
11	CHCCHCH* + H* ↔ CH_2CHCCH*	0	4.52
12	CHCCHCH* + H* ↔ CHCHCHCH*	1.02	3.55
13	CHCCHCH* + H* ↔ CH_2CCHCH*	0.17	2.82
14	CH_2CH* + CHC* ↔ CH_2CHCCH*	0	6.05
15	CH_2CH* + CHC* ↔ CHCHCHCH*	2.59	3.3
16	CH_2CH* + CHC* ↔ CH_2CCHCH*	1.51	2.34
17	CHCH* ↔ CCH_2*	1.2	1.32
18	CCH_2* + CHCH* ↔ CH_2CHCCH*	0.17	3.6
19	CCH_2* + CHCH* ↔ CHCHCHCH*	0.49	3.6
20	CCH_2* + CHCH* ↔ CH_2CCHCH*	0.14	3.37
21	CH_2CCHCH* ↔ CHCHCHCH*	2.46	2.34
22	CH_2CHCCH* ↔ CHCHCHCH*	2.82	2.5
23	CHCHCHCH* + CHCH* ↔ C_6H_6*	0.86	4.42
24	CHCH* + H_2O* ↔ CH_2CHOH*	0.13	1.95
25	CH_2CH* + H_2O* ↔ CH_2CHOH* + H*	2.69	2.6
26	CH_2CHOH* ↔ CH_3CHO*	0.39	1.27
27	CCH2* + H_2O* ↔ CH_2CHOH*	0.89	1.41
28	CHC* + H_2O* ↔ CH_2COH*	1.13	0.12
29	CH_2COH* ↔ CH_3CO*	1.37	0.98
30	CH_2COH* ↔ CH_2CHO*	0.62	1.32
31	CH_3CO* + H* ↔ CH_3CHO*	0.45	0.01
32	CH_2CHO* + H* ↔ CH_3CHO*	0.44	
33	CHCH* + * → * + CHCH*	0.22	
34	H* + * → * + H*	0.38	
35	CHC* + * → * + CHC*	0.17	
36	CH_2CH * + * → * + CH_2CH*	0.28	
37	$CH_3COOCHCH_2$* → $CH_3COOCHCH_2$(g) + *	0.21	
38	CH_2CHCCH* → CH_2CHCCH(g) + *	1.13	
39	C_6H_6* → C_6H_6(g) + *	1.16	
40[b]	CH_3CHO* → CH_3CHO(g) + *	1.26	
41	CH_3CHO* ↔ CH_2CHO* + H*	1.32	0.74

42	$CH_3CHO^* + CH_2CHO^* \leftrightarrow CH_3CHOCH_2CHO^*$	0.94	3.28
43	$CH_3CHOCH_2CHO^* + H^* \leftrightarrow CH_3CHOHCH_2CHO^*$	0.46	0.08
44	$CH_3CHOHCH_2CHO^* \leftrightarrow CH_3CHOHCHCHO^* + H^*$	0.53	0.12
45	$CH_3CHOHCHCHO^* \leftrightarrow CH_3CHCHCHO^* + OH^*$	1.75	1.04
46	$CH_2CHO^* + CCH_2^* \leftrightarrow CH_2CHCH_2CHO^*$	2.11	4.06
47	$CH_2CCH_2CHO^* \leftrightarrow CH_2CHCHCHO^*$	1.67	0.26
48	$CH_2CHCHCHO^* + H^* \leftrightarrow CH_3CHCHCHO^*$	0.25	1.49

[a] No. 1-40 data comes from previous research work[1-4];

[b] No. 41-48 data come from this research work;

[c] The pre-exponential factor for the surface catalytic reaction is10^{13} s^{-1}.

$E_{a.f}$ (eV) and $E_{a.r}$ (eV) represent the forward activation energy barrier and reverse activation energy barrier, respectively. The "↔" symbol in elementary reaction indicates that the forward and reverse directions are both considered in simulations. The "→" symbol indicates that only the forward reaction is considered.

Table 2 Kinetic Model of Homogeneous Reaction of Acetylene

No.	Elementary reaction	A	Ea/cal/mole
1	$C_2H_2 \rightarrow CCH_2$	4.03E+14	45261
2	$C_2H_2+CCH_2 \rightarrow VA$	9.21E+16	33024
3	$C_2H_2+CCH_2 \rightarrow MCP$	3.44E+17	13323
4	$MCP \rightarrow VA$	8.24E+16	48721
5	$\cdot CHCHCHCH\cdot \rightarrow CBD$	2.58E+14	79235
6	$MCP+C_2H_2 \rightarrow C_6H_6\text{-}1$	1.19E+14	13825
7	$C_6H_6\text{-}1 \rightarrow C_6H_6\text{-}2$	3.64E+14	56334
8	$C_6H_6\text{-}2 \rightarrow C_6H_6\text{-}3$	8.76E+15	74507
9	$C_6H_6\text{-}4 \rightarrow C_6H_6\text{-}5$	2.56E+16	49143
10	$C_6H_6\text{-}5 \rightarrow BEN$	9.32E+16	12380
11	$VA \rightarrow C_4H_4\text{-}1$	1.08E+10	85530
12	$C_4H_4\text{-}1 +C_2H_2 \rightarrow C_6H_6\text{-}L$	3.78E+16	16235
13	$C_6H_6\text{-}L \rightarrow IM5$	4.12E+15	38055
14	$C_2H_2+C_2H_2 \rightarrow \cdot CHCHCHCH\cdot$	1.60E+13	61056
15	$\cdot CHCHCHCH\cdot \rightarrow VA$	3.45E+17	20550
16	$C_2H_2+C_2H_2 \rightarrow C_4H_2+H_2$	1.14E+17	108844
17	$VA \rightarrow C_4H_2+H_2$	8.34E+15	74120
18	$C_2H_2+C_2H_2 \rightarrow CBD$	1.19E+13	53566
19	$CBD+C_2H_2 \rightarrow C_6H_6\text{-}6$	2.82E+13	25932
20	$C_6H_6\text{-}6 \rightarrow C_6H_6\text{-}7$	3.45E+17	20550
21	$C_6H_6\text{-}7 \rightarrow BEN$	5.87E+15	31319
22	$C_2H\cdot+C_2H_2 \rightarrow C_4H_3\cdot$	4.80E+15	4577
23	$C_2H\cdot+C_6H_2 \rightarrow C_8H_2+H\cdot$	4.64E+14	38188
24	$C_2H\cdot+C_4H_2 \rightarrow C_6H_2+H\cdot$	2.16E+11	12547
25	$C_2H_2+C_2H_2 \rightarrow C_4H_3\cdot+H\cdot$	1.76E+13	59303
26	$C_2H_2+C_2H_3\cdot \rightarrow VA+H\cdot$	2.64E+13	3505
27	$C_2H_2+C_4H_5\cdot \rightarrow N\text{-}C_6H_7\cdot$	8.48E+12	8490
28	$C_2H_2+H\cdot \rightarrow C_2H\cdot+H_2$	6.87E+16	32468
29	$C_2H_3\cdot+H\cdot \rightarrow C_2H_4$	9.80E+15	0
30	$VA+H\cdot \rightarrow C_4H_5\cdot$	1.30E+16	47487
31	$VA \rightarrow C_2H_3\cdot+C_2H\cdot$	1.41E+18	141745
32	$VA \rightarrow C_4H_3\cdot+H\cdot$	1.30E+16	86478
33	$c\text{-}C_6H_7\cdot \rightarrow BEN+H\cdot$	1.30E+16	29295
34	$C_2H_2+H\cdot \rightarrow C_2H_3\cdot$	5.49E+12	6051

35	$C_2H_2 \rightarrow C_2H\cdot+H\cdot$	4.03E+18	136829
36	$H\cdot+H\cdot \rightarrow H_2$	5.50E+16	0
37	$N\text{-}C_6H_7\cdot \rightarrow c\text{-}C_6H_7\cdot$	2.70E+14	3556
38	$C_2H_2+C_6H_5\cdot \rightarrow C_8H_6+H\cdot$	7.58E+12	29965
39	$C_2H_2+C_8H_5\cdot \rightarrow C_{10}H_6+H\cdot$	3.42E+14	3649
40	$H\cdot+BEN \rightarrow C_6H_5\cdot+H_2$	7.69E+13	17707
41	$H\cdot+C_8H_6 \rightarrow C_8H_5\cdot+H_2$	1.00E+11	8366
42	$H\cdot+VA \rightarrow C_4H_3\cdot+H_2$	3.62E+13	34162
43	$H\cdot+C_4H_3\cdot \rightarrow C_4H_2+H_2$	1.00E+13	0
44	$BEN \rightarrow C_6H_5\cdot+H\cdot$	7.00E+18	101942
45	$C_2H\cdot+M \rightarrow C_2+H\cdot+M$	4.07E+16	137870
46	$C_4H_2 \rightarrow C_4H\cdot+H\cdot$	2.17E+14	131679
47	$2C_6H_5\cdot \rightarrow C_{12}H_{10}$	9.23E+15	0
48	$C_6H_5\cdot+C_2H_3\cdot \rightarrow C_8H_8$	9.23E+15	0
49	$C_2H_4+M \rightarrow C_2H_3\cdot+H\cdot+M$	1.45E+16	81800
50	$C_2H_4+H \rightarrow C_2H_3\cdot+H_2$	6.92E+14	14500
51	$C_2H_3\cdot+C_2H_2 \rightarrow C_4H_5\cdot$	1.10E+12	4000
52	$C_6H_2 \rightarrow C_6H\cdot+H\cdot$	7.76E+14	120000
53	$C_2H_3\cdot+C_4H_2 \rightarrow VA+C_2H\cdot$	3.02E+13	23000
54	$C_2H_3\cdot+VA \rightarrow C_2H_4+C_4H_3\cdot$	5.01E+11	16300
55	$C_6H_5\cdot+BEN \rightarrow C_{12}H_{10}+H\cdot$	6.31E+11	11000
56	$BEN+C_2H\cdot \rightarrow C_8H_6+H\cdot$	1.00E+12	0
57	$C_4H_3\cdot \rightarrow C_4H_2+H\cdot$	1.00E+12	49000
58	$C_4H\cdot+C_2H_2 \rightarrow C_6H_2+H\cdot$	2.00E+13	0
59	$C_2H_3\cdot+VA \rightarrow BEN+H\cdot$	3.98E+11	0
60	$MCP \rightarrow C_4H_3\cdot+H\cdot$	2.88E+16	124262
61	$CBD \rightarrow C_4H_3\cdot+H\cdot$	2.52E+15	100873
62	$C_4H_4\text{-}1 \rightarrow C_4H_3\cdot+H\cdot$	2.52E+17	90873
63	$C_4H_3\cdot+C_2H\cdot \rightarrow C_6H_4$	3.61E+13	0
64	$C_4H_3\cdot+C_2H_2 \rightarrow C_6H_5\text{-}L\cdot$	2.62E+13	10583
65	$C_6H_5\text{-}L\cdot \rightarrow C_6H_5\cdot$	2.71E+14	19004
66	$C2H_2+C_4H_3\cdot \rightarrow VA+C_2H\cdot$	3.01E+12	27900
67	$C_4H\cdot \rightarrow C_4+H\cdot$	1.99E+14	116000
68	$C_4H_5\cdot+C_2H_3\cdot \rightarrow C_6H_6+H_2$	1.00E+15	0
69	$C_6H_2 \rightarrow C_2H\cdot+C_4H\cdot$	3.09E+16	145000
70	$C_8H_2 \rightarrow C_2H\cdot+C_6H\cdot$	3.09E+16	145000
71	$C_8H_2 \rightarrow C_4H\cdot+C_4H\cdot$	3.09E+16	145000
72	$C_6H\cdot \rightarrow C_6+H\cdot$	2.17E+14	111679
73	$H\cdot+C_2H_3\cdot \rightarrow H_2+C_2H_2$	9.64E+13	0
74	$CCH_2 \rightarrow H\cdot+C_2H\cdot$	9.64E+13	111942
75	$2C_2H_3\cdot \rightarrow C_2H_4+C_2H_2$	9.60E+11	0
76	$C_2H_3\cdot+C_2H_3\cdot \rightarrow C_4H_6$	7.00E+57	17629
77	$C_6H_5\cdot+C_2H\cdot \rightarrow C_8H_6$	9.60E+13	0
78	$C_6H_5\text{-}L\cdot \rightarrow H\cdot+C_2H_2+C_4H_2$	4.30E+12	77294
79	$C_2H_2+C_4H_5\cdot \rightarrow H+C_6H_6\text{-}L\cdot$	1.37E+16	8896
80	$C_2H_2+VA \rightarrow C_2H\cdot+C_4H_5\cdot$	1.00E+14	95000
81	$C_2H_2+VA \rightarrow C_2H_3\cdot+C_4H_3\cdot$	3.00E+14	73000
82	$C_4H_6 \rightarrow H_2+VA$	2.50E+15	94700
83	$VA+VA \rightarrow C_4H_5\cdot+C_4H_3\cdot$	5.00E+16	81500
84	$VA+VA \rightarrow C_2H_2+C_6H_6\text{-}L$	2.50E+14	44000
85	$C_2H_2+C_4H_5\cdot \rightarrow H\cdot+BEN$	1.37E+16	8896
86	$C_2H_3\cdot+C_4H_3\cdot \rightarrow BEN$	1.00E+13	0
87	$C_2H_3\cdot+C_4H_2 \rightarrow C_6H_5\cdot$	5.00E+11	6000
88	$C_4H_5\cdot+C_2H_3\cdot \rightarrow C_6H_8$	6.00E+12	0

89	$C_2H_2+C_6H_5\cdot \rightarrow C_2H\cdot+BEN$	7.40E+17	6728
90	$C_4H_6+C_6H_5\cdot \rightarrow C_4H_5\cdot+BEN$	8.88E+08	5707
91	$C_2H_3\cdot+BEN \rightarrow C_2H_4+C_6H_5\cdot$	1.08E+06	7460
92	$C_2H_2+C_4H_2 \rightarrow C_2H\cdot+C_4H_3\cdot$	3.00E+14	97000
93	$C_4H_5\cdot+C_4H_2 \rightarrow C_2H\cdot+C_6H_6$-L	5.00E+11	5000
94	$2C_4H_2 \rightarrow H_2+C_8H_2$	2.50E+14	44000
95	$C_4H_2+C_6H_2 \rightarrow C_2H_2+C_8H_2$	6.00E+15	44000
96	$C_2H_2 \rightarrow CH\cdot+CH\cdot$	4.68E+16	230000
97	$CH\cdot+C_2H_2 \rightarrow C_3H_3\cdot$	3.90E+14	15820
98	$C_3H_3\cdot \rightarrow C_3H_2\cdot+H\cdot$	1.31E+13	97000
99	$C_3H_2\cdot \rightarrow C_3+H_2$	5.69E+12	106000
100	$C_3H_2+C_2H_2 \rightarrow C_5H_4$	5.00E+12	15847
101	$C_3H_3\cdot+C_2H_2 \rightarrow C_5H_5\cdot$	3.40E+10	12800
102	$C_5H_4+H\cdot \rightarrow C_5H_5\cdot$	5.47E+14	0
103	$C_5H_5\cdot+H\cdot \rightarrow C_5H_6$	4.22E+13	0
104	$2C_3H_3\cdot \rightarrow C_6H_6$	1.81E+17	0

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