

Hydroxymethylcyclopropane on Oxygen-Covered Mo(110): A Radical Clock on a Surface.

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Supporting Information

Table 1. Results of Temperature-Programmed Reaction Spectrometry

Mass Fragmentation Patterns of Authentic Samples											
m/z	72	56	55	54	53	44	41	39	29	28	27
(C ₃ H ₅)CH ₂ -OH ^a	1	1	5	2	4	100	11	14	7	3	12
1-butene		42	23	3	7		100	53	18	45	42
1,3-butadiene			3	68	48			100	1	41	68
ethene									4	100	58
Experimental Mass Fragmentation Patterns for Sample of Hydroxymethylcyclopropane											
multilayer ^b	1	1	2	3	11	100	12	26	24	12	24
molecular layer ^c	1	2	3	5	5	100	13	25	20	16	22
products ^d		7	12	49	40		28	100	16	67	93
22:60:18 ^e		13	10	58	42		31	100	7	73	84

^a Gas-phase mass spectrum taken from ref 17. ^b Integrated over the multilayer peak at 200 K. ^c Integrated over the molecular layer peak at 250-350 K. ^d Integrated over the product peak at 350 - 620 K. ^e Calculated fragmentation pattern assuming a 22:60:18 mixture of 1-butene:1,3-butadiene:ethene.

Table 2. Vibrational Assignment for selected Infrared modes.

mode	(C ₃ H ₅)CH ₂ -OH ^a	c-C ₃ H ₅ -CH ₂ O-	C ₄ H ₇ O- ^b	C ₄ H ₇ -	HO-
v(C-O-Mo)		905	867(854)		
		936	939(930)		
v(C-O)	1027	1029	1042(1039)		
v(C-C) _{ring}	1213				
δ(CH ₂)				1243	
ring modes	1400	1393,1434			
v(C=C)			1645(1645)		
v(C-H)	2888-3090	3010	2936(2936)	2958	
			3089(3089)	2983	
v(O-H)	3672				3572

^a Gas-phase IR spectrum taken from ref 17. ^b Values for ¹⁸O-labeled surface are given in parenthesis.

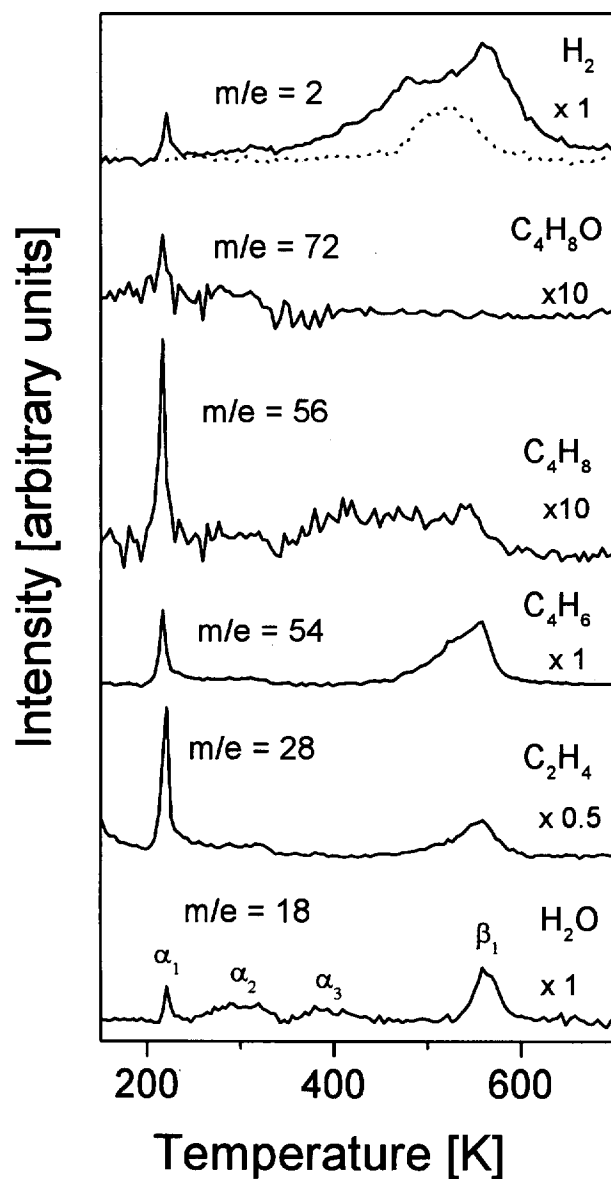


Figure 2. Temperature-programmed reaction spectrum of hydroxymethylcyclopropane on oxygen-covered Mo(110). The dotted line at $m/z = 2$ represents the trace obtained when a clean $2/3$ O-covered Mo(110) surface is heated to 760 K. The data are not corrected for fragmentation. All water peaks shift by two amu to $m/z = 20$ upon ^{18}O labeling of the surface. Only the β_1 peak appears at both $m/z = 18$ and 20, indicating some involvement of the hydroxymethylcyclopropane oxygen in water formation. Note the onset of the β_1 peak coincides with the formation of 1,3-butadiene.