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Pressure and temperature dependent kinetics and the reaction mechanism of Criegee intermediates with vinyl alcohol: a theoretical study

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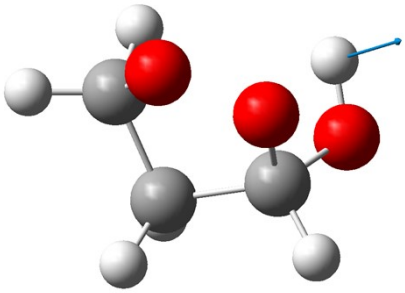


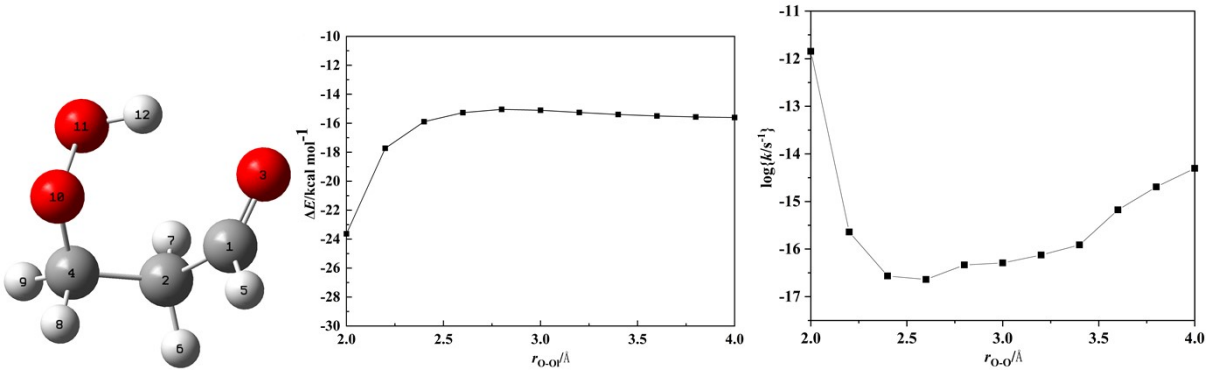
Figure S1 The vector of imaginary frequency in TS9

Table S1 Cartesian coordinates IM8 and TS9

IM8				TS9			
O	-1.335774	-0.760334	0.023423	O	-1.315497	-0.768930	0.071667
C	-1.236940	0.576576	0.472043	C	-1.215145	0.582548	0.478623
H	-2.225378	1.016780	0.346809	H	-2.210745	1.009678	0.364653
H	-0.945303	0.609675	1.529597	H	-0.897739	0.651673	1.526709
O	0.021479	-1.175126	-0.205695	O	0.026862	-1.174363	-0.271033
C	0.815263	-0.020728	-0.472069	C	0.818253	-0.015115	-0.476887
C	-0.165977	1.151037	-0.438002	C	-0.172388	1.145218	-0.469422
H	1.306604	-0.150873	-1.436081	H	1.350014	-0.132919	-1.421182
H	-0.578833	1.330309	-1.431271	H	-0.602601	1.284058	-1.462007
H	0.319963	2.050592	-0.065799	H	0.305677	2.061551	-0.130339
O	1.837345	0.063232	0.474937	O	1.794773	0.081392	0.522443
H	1.464473	-0.119966	1.343598	H	1.421970	-0.254737	1.343658

Table S2 The rate constants (in cm^3 $molecule^{-1}$ s^{-1}) of each entrance channels calculated by the traditional transition state theory at 300 K and 760 torr

reaction channels	1,4-insertion-a	1,4-insertion-b	cycloaddition	insertion - OH	insertion- CH	k_{total}
CH_2OO+*syn*-VA	1.61E-11	1.34E-11	9.11E-16	1.85E-14	1.82E-22	2.95E-11
CH_2OO+*anti*-VA	4.19E-16	3.11E-15	1.67E-13	3.53E-14	2.57E-17	2.06E-13



(a) (b) (c)

Figure S2 The lables in IM1(a), Minimum energy path (b) and the variation of TST rate constants (c) for the IM1→$CHOCH_2CH_2O$ + OH pathway

First, the geometries were optimized along the IM1→$CHOCH_2CH_2O$ + OH pathway at the M06-2X/def2TZVP level of theory by varying the dissociating O-O bond distance point by point from 2.0 to 4.0 Å, with an interval of 0.2 Å. The bond angle O10O11H12 and dihedral angle C4O10O11H12 are fixed to avoid OH rotation. Second, we calculate the corresponding energies with HL method based on the optimized geometries, and the minimum energy path (MEP) is shown in Figure S2(b). Since the above reaction is a homolytic cleavage process from a closed shell to an open shell system, we use "guess = mix" to mix the HOMO and LUMO. Third, the dissociation rate constants were calculated point by ponint along the MEP by the TST theory, as shown in Figure S2(c), the minima of TST appears at the point of $r_{O\text{-}O}$=2.6 Å. The corresponding geometry is taken as variational transition state and used to the subsequent master equation

calculation.