Reactivity of CHI_3 with OH Radicals. X-Abstraction Reaction Pathways (X = H, I), Atmospheric Chemistry and Nuclear Safety

Mária Sudolská[1], Florent Louis[2,], Ivan Černušák[1,*]*

[1] Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CH1, 84215 Bratislava, Slovakia, cernusak@fns.uniba.sk (I.Č.)

[2] PhysicoChimie des Processus de Combustion et de l'Atmosphère (PC2A), UMR 8522 CNRS/Lille1, Université Lille 1 Sciences et Technologies, Cité Scientifique, Bât. C11/C5, 59655 Villeneuve d'Ascq Cedex, France, florent.louis@univ-lille1.fr

(Supporting Information)

Table S1. Reactants and products: MP2/cc-pVTZ optimized geometry parameters[a].

Species	Parameter	MP2/cc-pVTZ	Literature
OH	r (OH)	0.967	0.971[b]
CHI_3	r (CH)	1.082	1.09[c]
	r (CI)	2.129	2.12[c]
	θ (HCI)	106.3	105.7[c]
	θ (ICI)	112.5	113.0[c]
	ϕ (HCII)	115.9	
H_2O	r (OH)	0.959	0.958[d]
	θ (HOH)	103.5	104.5[d]
HOI	r (OH)	0.967	0.968[e]
	r (OI)	1.992	1.994[e]
	θ (HOI)	103.0	103.9[e]
CI_3	r (CI)	2.059	
	θ (ICI)	118.4	
	ϕ (ICII)	154.9	
CHI_2	r (CH)	1.078	
	r (CI)	2.039	
	θ (HCI)	116.6	
	θ (ICI)	122.3	
	ϕ (HCII)	155.3	

[a] Bond lengths are in Å; bond angles θ and dihedral angles ϕ are in deg.

[b] Chase[1]. [c] Kudchadker and Kudchadker[2]. [d] CRC Handbook of Chemistry and Physics[3]. [e] Ozeki et al.[4].

Table S2. Transition states and molecular complexes: MP2/cc-pVTZ optimized Cartesian coordinates, in a.u.

H-abstraction pathway			
MCR_{Hab}			
H	–0.473542	1.415568	0.000000
C	–0.211019	0.365424	0.000000
I	–2.021598	–0.746596	0.000000
I	0.939603	0.059446	1.766165
I	0.939603	0.059446	–1.766165
O	0.939603	3.351258	0.000000
H	1.769643	2.850076	0.000000
TS_{Hab}			
H	–0.007504	–0.003779	1.540354
C	–0.007155	0.004017	0.367998
I	0.221727	2.036131	–0.177121
I	1.622552	–1.215179	–0.234292
I	–1.893925	–0.806838	–0.145396
O	0.193143	–0.060498	2.864371
H	1.136535	–0.284324	2.847575
MCP_{Hab}			
H	0.422403	2.387462	0.000000
C	–0.019990	0.064897	0.000000
I	–2.077260	0.132112	0.000000
I	0.946881	–0.360297	1.768607
I	0.946881	–0.360297	–1.768607
O	0.946881	3.193782	0.000000
H	1.847897	2.862428	0.000000

Table S2. Transition states and molecular complexes: MP2/cc-pVTZ optimized Cartesian coordinates, in a.u. (continuation).

I-abstraction pathway			
MCR_{Iab}			
H	1.637658	0.549703	0.000000
C	0.572579	0.356038	0.000000
I	0.329139	–1.756865	0.000000
I	–0.187451	1.267662	1.769819
I	–0.187451	1.267662	–1.769819
O	–0.187451	–4.868772	0.000000
H	–1.148162	–4.994052	0.000000
TS_{Iab}			
H	0.419162	–0.019197	1.749711
C	0.495708	–0.009864	0.669978
I	–1.953680	–0.091889	–0.005635
I	1.562279	–1.637282	–0.042912
I	0.976794	1.874026	–0.047127
O	–3.822329	–0.766167	–0.004308
H	–3.840577	–1.469614	–0.664383
MCP_{Iab}			
H	–0.496496	–0.002049	1.744003
C	–0.748331	0.001197	0.693191
I	2.186465	–0.018919	0.031807
I	–1.381780	1.793607	–0.052311
I	–1.422721	–1.773284	–0.056232
O	4.168559	–0.103615	–0.160361
H	4.393878	0.749388	–0.553233

Table S3. Calculated[a] unscaled vibrational frequencies for reactants and products.

Species	Vibrational frequencies (cm^{-1})[b]
OH	3821
	3735[c]
CHI_3	106, 106, 161, 449, 632, 632, 1098, 1098, 3191
	111, 111, 153, 427, 573, 573, 1065, 1065, 2974[d]
H_2O	1652, 3855, 3976
	1595, 3651, 3756[c]
HOI	604, 1116, 3797
	575[e], *1068*[f], *3626*[h]
CI_3	112, 112, 173, 230, 754, 754
	693, *693*[i]
CHI_2	133, 339, 551, 764, 1152, 3253
	716, 1106[i]

[a] MP2/cc-pVTZ. [b] Experimental values of vibrational frequencies are in italics. [c] Chase[1]. [d] Kudchadker and Kudchadker[2]. [e] Walker et al.[5]. [f] Barnes et al.[6]. [h] Klaasen et al.[7]. [i] Smith and Andrews[8].

Table S4. Calculated[a] unscaled vibrational frequencies for transition states.

Species	Vibrational frequencies (cm^{-1})
TS_{Hab}	**1742i**, 20, 70, 90, 108, 110, 159, 307, 615, 655, 725, 882, 1014, 1303, 3790
TS_{Iab}	**210i**, 57, 68, 91, 123,172,189, 459, 695, 785, 793, 1072, 1135, 3206, 3825

[a] MP2/cc-pVTZ.

Table S5. Calculated[a] unscaled vibrational frequencies for molecular complexes on the reactant side.

Species	Vibrational frequencies (cm^{-1})
MCR_{Hab}	30, 32, 52, 99, 106, 109, 163, 248, 454, 629, 641, 1106, 1126, 3196, 3793
MCR_{Iab}	15, 31, 44, 84, 109, 109, 162, 205, 453, 631, 639, 1100, 1101, 3186, 3805

[a] MP2/cc-pVTZ.

Table S6. Calculated[a] unscaled vibrational frequencies for molecular complexes on the product side.

Species	Vibrational frequencies (cm^{-1})
MCP_{Hab}	23, 32, 41, 88, 112, 112, 146, 189, 232, 251, 748, 750, 1649, 3821, 3942
MCP_{Iab}	30, 40, 44, 56, 65, 135, 152, 487, 602, 701, 747, 1103, 1150, 3229, 3813

[a] MP2/cc-pVTZ.

Table S7. Literature standard enthalpy of formation at 298 K, in kJ mol^{-1}.

Species	$\Delta_f H°_{298K}$	Reference
OH	38.987 ± 1.210	Chase[1]
CHI_3	208.5 ± 9.9	Marshall et al.[9]
	251.0 ± 1.4	Carson et al.[10]
	210.9 ± 4.2	Kudchadker and Kudchadker[2, 11]
H_2O	–241.826 ± 0.042	Chase[1]
CI_3	369.1 ± 9.9	Marshall et al.[9]
	424.9 ± 2.8	Seetula[12]
HOI	–69.0 ± 3.7	Šulková et al.[13]
	–59.2 ± 3.3	Marshall[14]
CHI_2	298.3	Louis et al.[15]
	290.4 ± 9.9	Marshall et al.[9]
	314.4 ± 3.3	Seetula[12]

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