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SUPPORTING INFORMATION

Table 1S: MP2/6-311G(2d,2p) optimized geometry parameters for halomethanes

Species	Parameter [a)]
CH_2FBr	r_{CH} = 1.080, r_{CF} = 1.361, r_{CBr} = 1.940, θ(HCH) = 112.6, θ(FCH) = 109.6, θ(BrCH) = 107.2, ϕ(FCHH) = 122.3, ϕ(BrCHH) = -117.6
$CHFBr_2$	r_{CH} = 1.079, r_{CF} = 1.349, r_{CBr} = 1.933, θ(FCH) = 109.9, θ(BrCH) = 107.8, ϕ(BrCHF) = 119.3
$CHFClBr$	r_{CH} = 1.079, r_{CF} = 1.347, r_{CCl} = 1.772, r_{CBr} = 1.935, θ(FCH) = 109.8, θ(ClCH) = 108.4, θ(BrCH) = 107.7, ϕ(ClCHF) = 119.7, ϕ(BrCHF) = -119.1
$CHCl_2Br$	r_{CH} = 1.077, r_{CCl} = 1.772, r_{CBr} = 1.938, θ(ClCH) = 108.0, θ(BrCH) = 106.7, ϕ(ClCHBr) = 119.7
$CHClBr_2$	r_{CH} = 1.077, r_{CCl} = 1.770, r_{CBr} = 1.937, θ(ClCH) = 108.2, θ(BrCH) = 107.0, ϕ(ClCHBr) = 120.3

[a)] Bond lengths are in Angstroms, bond angles θ and dihedral angles ϕare in degrees.

Table 2S: MP2/6-311G(2d,2p) optimized geometry parameters for halomethyl radicals

Species	Parameter [a)]
$CHFBr$	r_{CH} = 1.078, r_{CF} = 1.331, r_{CBr} = 1.876, θ(FCH) = 113.9, θ(BrCH) = 116.1, ϕ(BrCHF) = 137.1
$CFBr_2$	r_{CF} = 1.325, r_{CBr} = 1.889, θ(BrCF) = 113.2, ϕ(BrCFBr) = 137.7
$CFClBr$	r_{CF} = 1.325, r_{CCl} = 1.728, r_{CBr} = 1.889, θ(ClCF) = 113.0, θ(BrCF) = 113.4, ϕ(BrCFCl) = 137.0
CCl_2Br	r_{CCl} = 1.719, r_{CBr} = 1.877, θ(ClCBr) = 117.0, ϕ(ClCBrCl) = 145.0
$CClBr_2$	r_{CCl} = 1.718, r_{CBr} = 1.877, θ(BrCCl) = 116.8, ϕ(BrCClBr) = 145.9

[a)] Bond lengths are in Angstroms, bond angles θ and dihedral angles ϕare in degrees.

Table 3S: MP2/6-311G(2d,2p) optimized geometry parameters for the transition states in the series of reactions OH with CH_2FBr, $CHFBr_2$, $CHFClBr$, $CHCl_2Br$ and $CHClBr_2$

Parameter [a]	OH + CH_2FBr	OH + $CHFBr_2$	OH + CHFClBr	OH + $CHCl_2Br$	OH + $CHClBr_2$
r (C-H_R)	**1.190**	**1.186**	**1.189**	**1.183**	**1.182**
r (C-X)	1.081	1.346	1.345	1.922	1.757
r (C-Y)	1.355	1.918	1.755	1.761	1.921
r (C-Z)	1.914	1.918	1.919	1.761	1.927
r (O-H_R)	**1.296**	**1.296**	**1.291**	**1.299**	**1.300**
r (H-O)	0.966	0.967	0.967	0.967	0.967
θ (XCH)	109.1	108.2	108.1	104.1	107.4
θ (YCH)	108.2	106.7	107.5	107.4	104.3
θ (ZCH)	106.6	106.7	106.4	107.4	106.5
θ (OH_RC)	**160.3**	**162.0**	**162.7**	**170.8**	**171.3**
θ (HOH_R)	97.1	98.7	98.6	98.6	98.3
ϕ (YCHX)	120.4	118.9	119.2	119.5	119.9
ϕ (ZCHX)	-119.2	-118.9	-118.6	-119.5	-120.7
ϕ (OH_RCX)	272.2	0.0	-9.9	180.0	67.0
ϕ (HOH_RC)	-35.6	0.0	4.0	-0.1	11.0

[a] Bond lengths are in Angstroms, bond angles θ and dihedral ϕ are in degrees; the hydrogen atom involved in H-atom abstraction is noted H_R

Table 4S: Calculated MP2/6-311G(2d,2p) vibrational frequencies (in cm^{-1}) for halomethanes and halomethyl radicals

Species	Vibrational frequencies (cm^{-1})
CH_2FBr	316, 660, 961, 1104, 1276, 1372, 1529, 3160, 3248
$CHFBr_2$	174, 301, 361, 628, 719, 1106, 1213, 1340, 3218
CHFClBr	228, 318, 426, 667, 787, 1112, 1244, 1351,3220
$CHCl_2Br$	219, 226, 334, 609, 739, 779, 1212, 1249, 3232
$CHClBr_2$	170, 204, 283, 571, 677, 758, 1188, 1228, 3233
CHFBr	339, 676, 820, 1189, 1323, 3236 *650, 1149, 1266* [a]
$CFBr_2$	178, 315, 384, 501, 817, 1176 *782, 1136* [a]
CFClBr	233, 333, 446, 554, 878, 1182
CCl_2Br	228, 240, 339, 440, 845, 889 *835, 888* [a]
$CClBr_2$	179, 214, 303, 386, 793, 860 *783, 856* [a]

The experimental values of the vibrational frequencies are in italics. These values are taken from [a] ref. 1S

Table 5S: Calculated MP2/6-311G(2d,2p) vibrational frequencies (in cm^{-1}) for transition states

Species	Vibrational frequencies (cm^{-1})
OH + CH_2FBr	**2184i**, 88, *128*, 171, 323, 518, 740, 856, 1014, 1121, 1311, 1552, 3200, 3814
OH + $CHFBr_2$	**2183i**, 64, *104*, 109, 174, 305, 340, 383, 754, 816, 881,1074, 1114, 1539, 3813
OH + CHFClBr	**2220i**, 71, *100*, 116, 226, 322, 365, 455, 804, 839, 887, 1098, 1121, 1534, 3813
OH + $CHCl_2Br$	**2174i**, *30*, 82, 108, 222, 228, 306, 423, 725, 775, 800, 876, 1109, 1380, 3808
OH + $CHClBr_2$	**2173i**, *32*, 78, 102, 172, 207, 267, 388, 666, 761, 777, 869, 1091, 1366, 3808

Vibrational frequencies indicated in italics correspond to the hindered rotation of the –OH group

REFERENCE FOR SUPPORTING INFORMATION:

1S) Jacox, M.E. Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules, J.Phys.Chem.Ref.Data, **1994**, Monograph N°3.