

Electronic Supplementary Information

Lewis acid-Activated Oxidation of Alcohols by Permanganate

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1. Materials

Caution: Care should be taken in handling Lewis acid/ MnO_4^- in organic solvents, since the system is very reactive. Although we have not encountered any problems so far, the amount of KMnO_4 used each time should be less than 50 mg. Potassium permanganate (Ajax Chemicals, AR) was used as received. Boron trifluoride acetonitrile complex solution ($\text{BF}_3 \cdot \text{CH}_3\text{CN}$) (Sigma, 15-18%) was stored at -20°C and was used without further purification. Scandium (III) triflate (Aldrich, 99%), calcium trifluoromethanesulfonate (Aldrich, 99.9%), zinc trifluoromethanesulfonate (Sigma-Aldrich, 98%), and barium trifluoromethanesulfonate (Aldrich, 98%) were stored in dry box and used without further purification. Methanol (Mecker, 99.9%), ethanol (Mecker, 99.9%), 2-propanol (sigma, 98%), cyclohexanol (Sigma, 99%), cyclobutanol (Aldrich, 99%), 2-heptanol (Riedel-deHaën, 98%), 1-heptanol (Aldrich, 98%), benzyl alcohol (Sigma, 99%), 1-phenylethanol (Aldrich, 98%), 4-chlorobenzyl alcohol (Riedel-deHaën, 99%) were used as received. Acetonitrile (Mecker, 99.9%) was stirred overnight with KMnO_4 and then distilled; it was distilled again over CaH_2 under argon.¹

2. Product analysis

The organic products resulting from the oxidation of alcohols by $\text{BF}_3 \cdot \text{CH}_3\text{CN}$ were determined as followed. A solution of $\text{BF}_3 \cdot \text{CH}_3\text{CN}$ (0.12 mmol) in CH_3CN was added with vigorous stirring to a solution of KMnO_4 (8×10^{-3} mmol) in CH_3CN containing a

known amount of alcohol (0.8 mmol). After 15 min 100 μL of H_2O were added to quench the reaction, and the resulting mixture was analyzed by GC and GC-MS using chlorobenzene as the internal standard. A Hewlett-Packard 5890 gas chromatograph with a DB-FFAP capillary column (30 mm \times 0.25 mm i.d.) was used. GC-MS measurements were carried out on an HP 6890 gas chromatograph interfaced to an HP 5975 mass selective detector.

3. Kinetics

The kinetics of the reaction were studied by using a Shimadzu UV1800 spectrophotometer and an Applied Photophysics SX-20 stopped-flow spectrophotometer. The concentrations of the alcohols were at least in 10-fold excess of that of MnO_4^- . Reactions were initiated by mixing a freshly prepared solution of KMnO_4 in CH_3CN with Lewis acid and alcohols in CH_3CN . The reaction progress was monitored by observing absorbance changes at 526 nm (λ_{max} of MnO_4^-). Pseudo-first-order rate constants, k_{obs} , were obtained by nonlinear least-squares fits of A_t vs time t according to the equation $A_t = A_f + (A_0 - A_f) \exp(-k_{\text{obs}} t)$, where A_0 and A_f are the initial and final absorbances, respectively.

4. Computational Study

The reaction mechanisms for oxidation of methanol and 1-phenyl-ethanol by the MnO_4^- and $\text{BF}_3 \cdot \text{MnO}_4^-$ have been theoretically studied by density functional theory. The structures and energies of all molecular species are calculated at the B3LYP level² with the LanL2DZ basis set³ for transition metal (Mn) and 6-311++G(d,p) basis set for the nonmetal atoms. The polarizable continuum model (PCM)⁴ is used to account for the solvent effects in acetonitrile. All calculations are performed with Gaussian 09 package of program.⁵ The potential energy surfaces for the oxidation of methanol by $[\text{MnO}_4]^-$ is shown in **Scheme 1**. As presented in **Schemes 1 to 3**, the optimized structures of the intermediates (INT) and transition states (TS) at gas phase and in solvent medium are fairly similar.

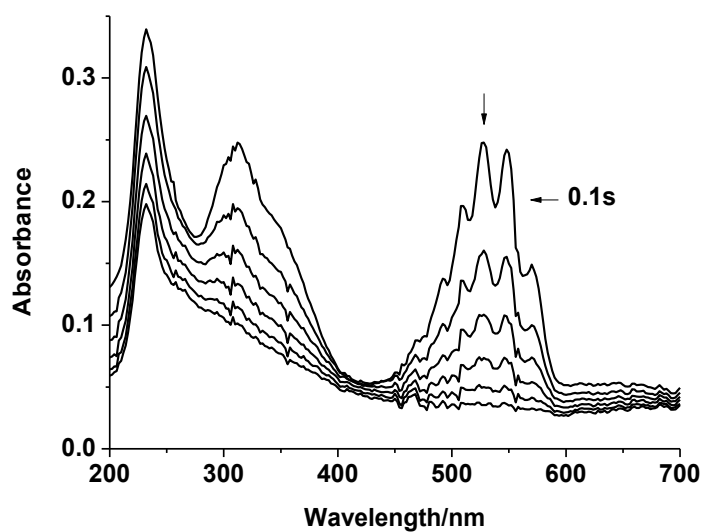


Fig.S1 Spectrophotometric changes for the BF_3 (4.0×10^{-3} M) activated oxidation of CH_3OH (1.0×10^{-3} M) by KMnO_4 (1.0×10^{-4} M) at 1 s intervals

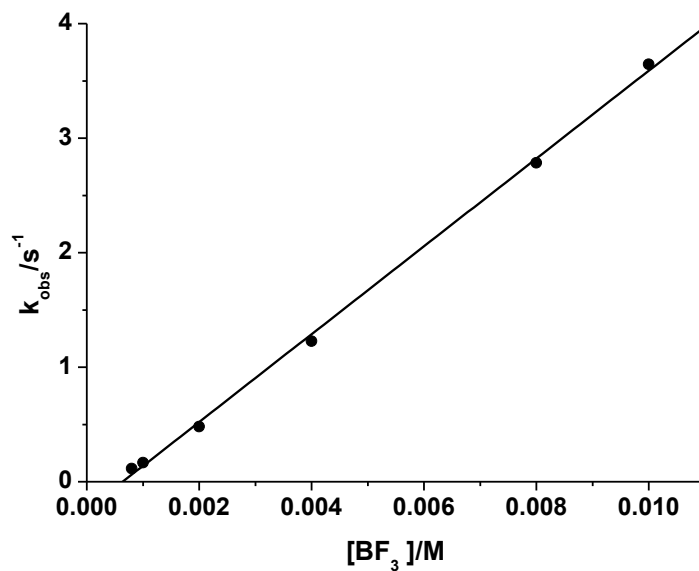


Fig.S2 Plot of k_{obs} vs $[\text{BF}_3]$ for the BF_3 activated oxidation of CH_3OH by KMnO_4 (1.0×10^{-4} M) at 298.0 K ($[\text{KMnO}_4] = 1.0 \times 10^{-4}$ M, $[\text{CH}_3\text{OH}] = 1.0 \times 10^{-2}$ M, slope = $(3.83 \pm 0.07) \times 10^2$, y-intercept = $-(2.45 \pm 0.37) \times 10^{-1}$, $r = 0.998$)

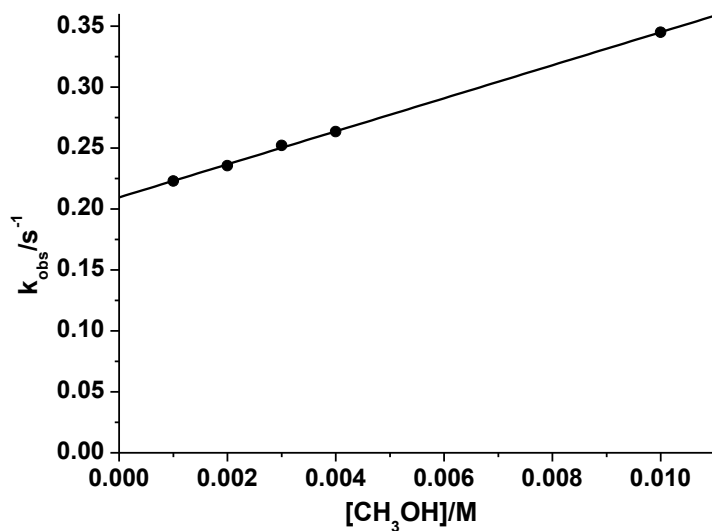


Fig.S3 Plot of k_{obs} vs $[\text{CH}_3\text{OH}]$ for the for the $\text{Sc}(\text{CF}_3\text{SO}_3)_3$ (1.0×10^{-3} M) activated oxidation of CH_3OH by KMnO_4 (1.0×10^{-4} M) at 298.0 K (slope = $(1.35 \pm 0.02) \times 10^1$, y-intercept = $(2.09 \pm 0.00) \times 10^{-1}$, $r = 0.999$)

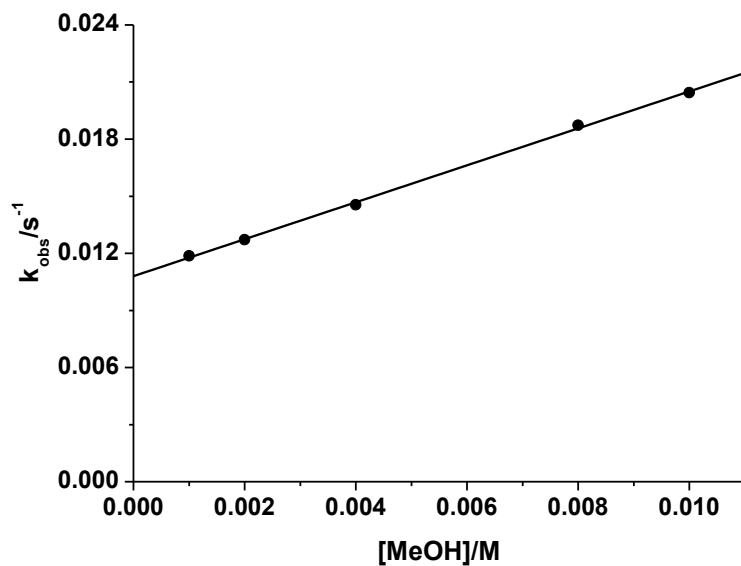


Fig.S4 Plot of k_{obs} vs $[\text{CH}_3\text{OH}]$ for the $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (1.0×10^{-3} M) activated oxidation of CH_3OH by KMnO_4 (1.0×10^{-4} M) at 298.0 K (slope = $(9.71 \pm 0.18) \times 10^{-1}$, y-intercept = $(1.08 \pm 0.01) \times 10^{-2}$, $r = 0.999$)

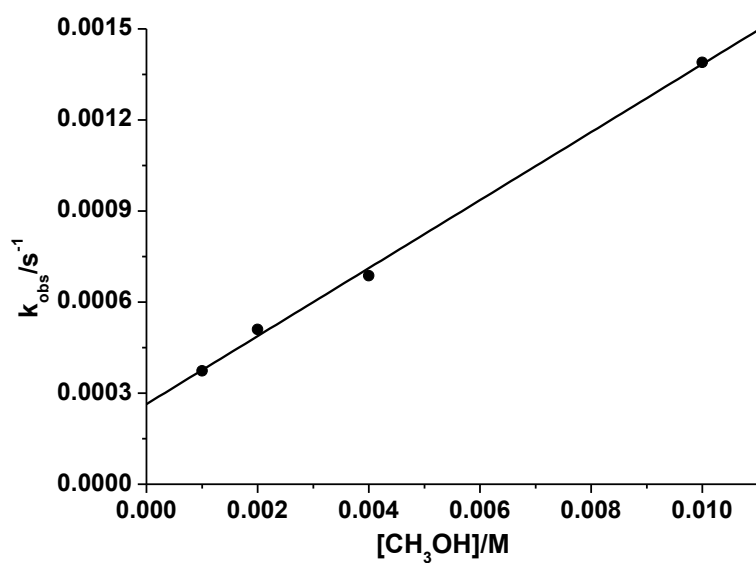


Fig.S5 Plot of k_{obs} vs $[\text{CH}_3\text{OH}]$ for the $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ (1.0×10^{-3} M) activated oxidation of CH_3OH by KMnO_4 (1.0×10^{-4} M) at 298.0 K (slope = $(1.12 \pm 0.03) \times 10^{-1}$, y-intercept = $(2.64 \pm 0.19) \times 10^{-4}$, $r = 0.997$)

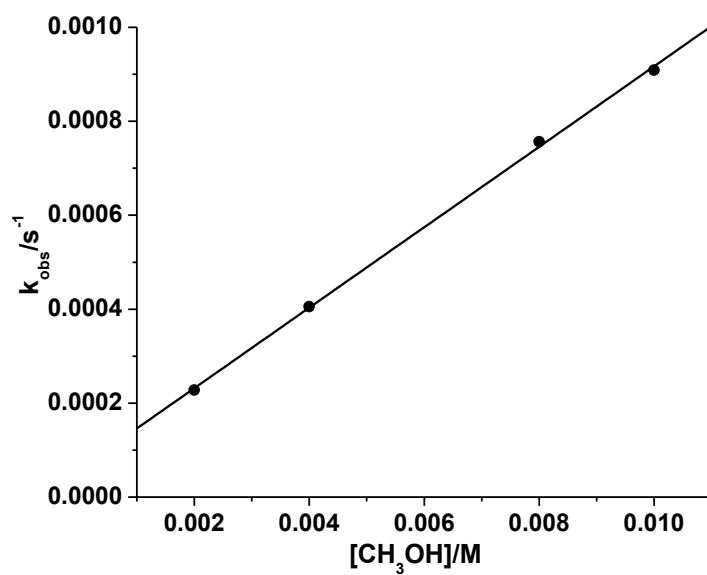
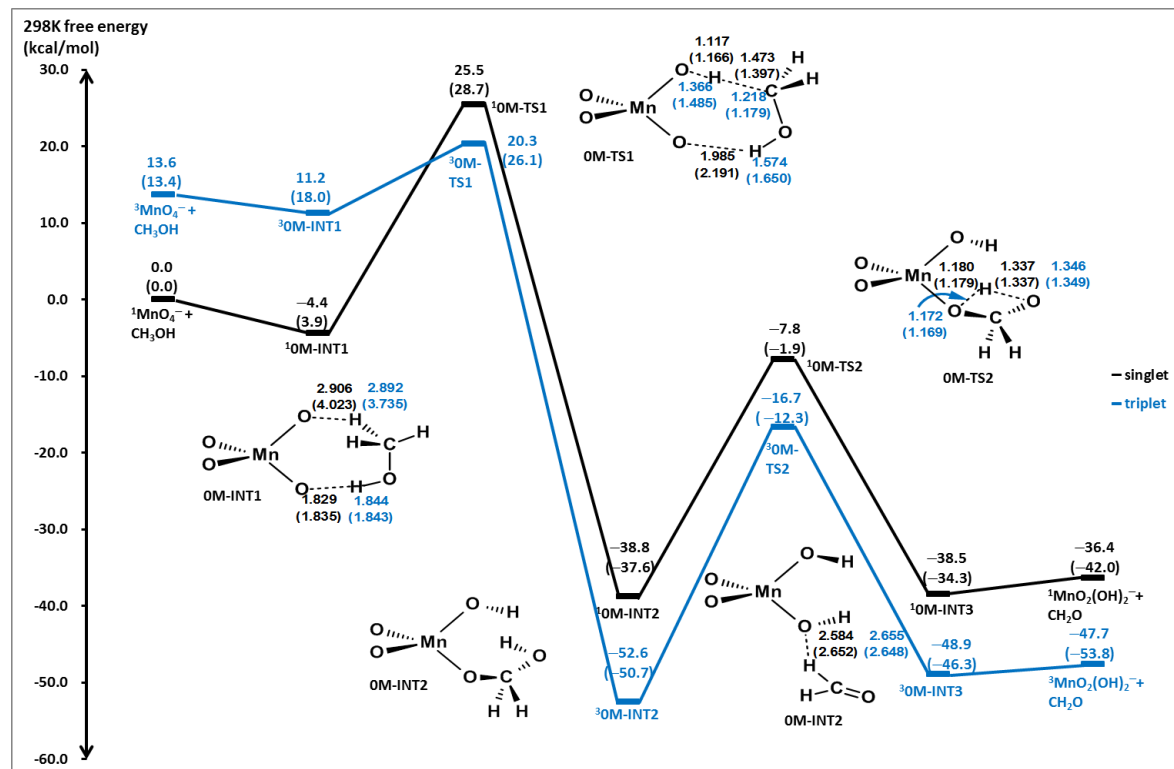
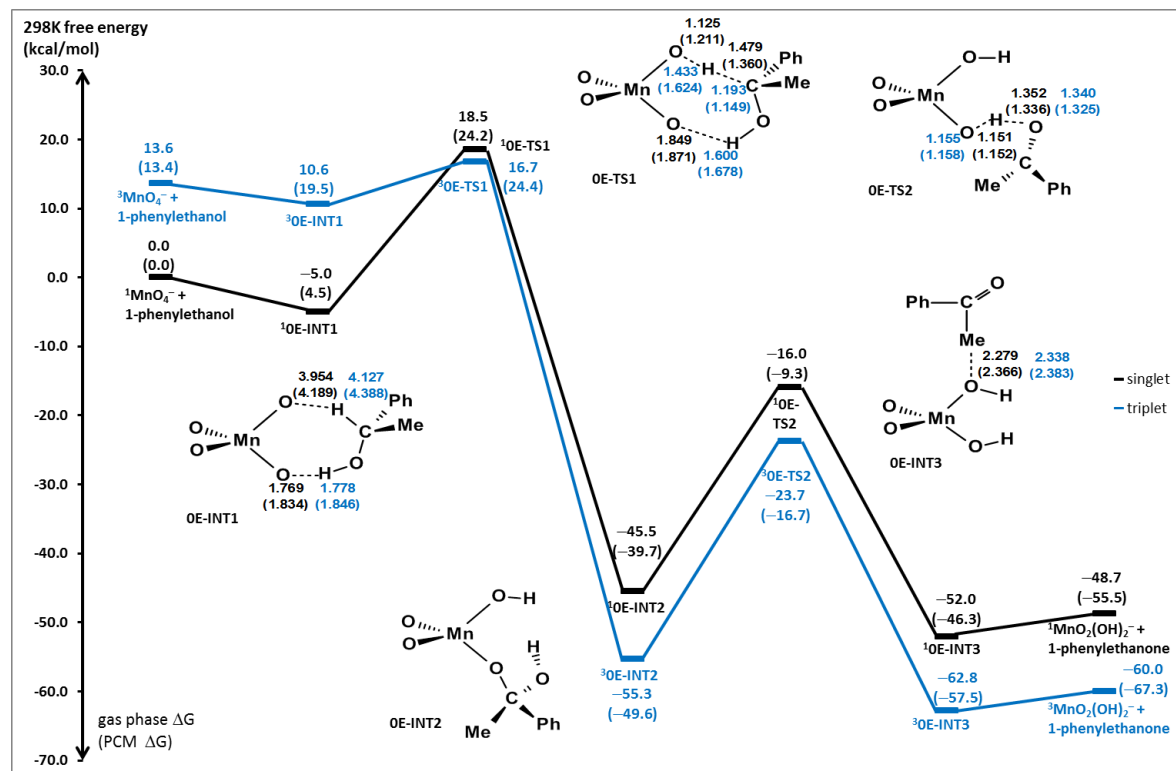


Fig.S6 Plot of k_{obs} vs $[\text{CH}_3\text{OH}]$ for the $\text{Ba}(\text{CF}_3\text{SO}_3)_2$ (1.0×10^{-3} M) activated oxidation of CH_3OH by KMnO_4 (1.0×10^{-4} M) at 298.0 K (slope = $(8.57 \pm 0.16) \times 10^{-2}$, y-intercept = $(6.04 \pm 1.08) \times 10^{-5}$, $r = 0.999$)

Scheme S1: Singlet and triplet potential energy surface for the oxidation of methanol by MnO_4^- at B3LYP level using LanL2DZ basis set for transition metal (Mn) and 6-311++G(d,p) basis set for nonmetal atoms. Relative 298 K Gibbs free energies at gas phase and in acetonitrile (in parentheses) are given in kcal/mol.



Scheme S2: Singlet and triplet potential energy surface for the oxidation of 1-phenylethanol by $[\text{BF}_3 \cdot \text{MnO}_4]^-$ at B3LYP level using LanL2DZ basis set for transition metal (Mn) and 6-311++G(d,p) basis set for nonmetal atoms. Relative 298 K Gibbs free energies at gas phase and in acetonitrile (in parentheses) are given in kcal/mol.



Scheme S3: Singlet and triplet potential energy surface for the oxidation of 1-phenylethanol by MnO_4^- at B3LYP level using LanL2DZ basis set for transition metal (Mn) and 6-311++G(d,p) basis set for nonmetal atoms. Relative 298 K Gibbs free energies at gas phase and in acetonitrile (in parentheses) are given in kcal/mol.

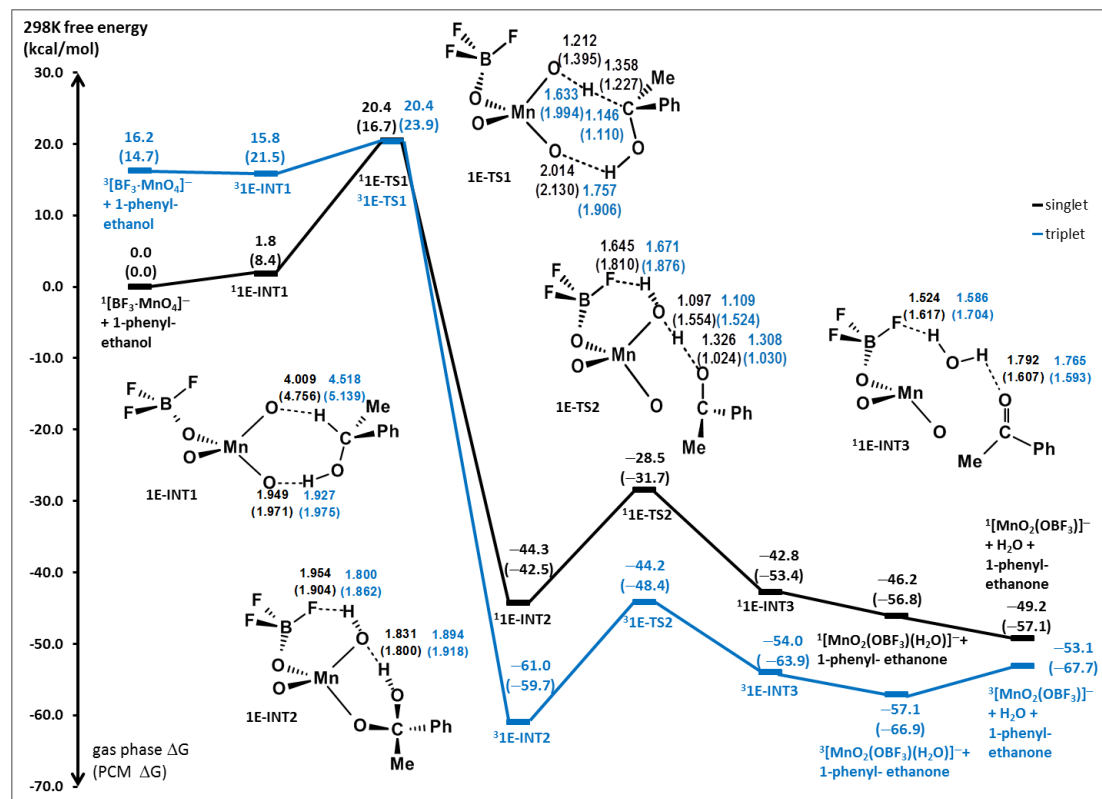


Table S1: Bond strength and hydride affinity of alpha C–H bond of alcohols at gas phase and in acetonitrile calculated at B3LYP/6-311++G(d,p) level.

Alcohol	C–H bond strength or hydride affinity (kcal/mol)			
	Gas phase		Acetonitrile (PCM)	
	ΔH_{298}°	ΔG_{298}°	ΔH_{298}°	ΔG_{298}°
RCH₂OH → RCHOH + H				
benzyl-alcohol	79.6	71.7	78.9	71.2
1-phenyl-ethanol	79.6	70.5	79.4	70.6
2-pentanol	89.7	80.8	90.0	81.0
2-propanol	89.7	80.9	90.0	81.2
ethanol	91.7	83.2	91.8	83.3
methanol	93.3	84.9	93.4	85.1
cyclohexanol (chair)	89.7	81.1	90.0	81.4
cyclohexanol (boat)	88.9	79.8	89.1	80.1
RCH₂OH → RCHOH⁺ + H⁻				
benzyl-alcohol	227.6	220.8	182.1	175.3
1-phenyl-ethanol	222.1	213.9	178.5	170.8
2-pentanol	230.4	222.1	179.9	171.7
2-propanol	234.3	225.9	181.0	172.6
ethanol	249.5	241.9	191.3	183.6
methanol	271.1	263.7	206.4	199.0
cyclohexanol (chair)	228.8	220.6	180.7	172.7
cyclohexanol (boat)	225.8	217.5	177.1	168.9

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