Supporting Information:

Highly regioselective hydride transfer, oxidative dehydrogenation, and hydrogen-atom abstraction in the thermal gas-phase chemistry of $[Zn(OH)]^+/C_3H_8$

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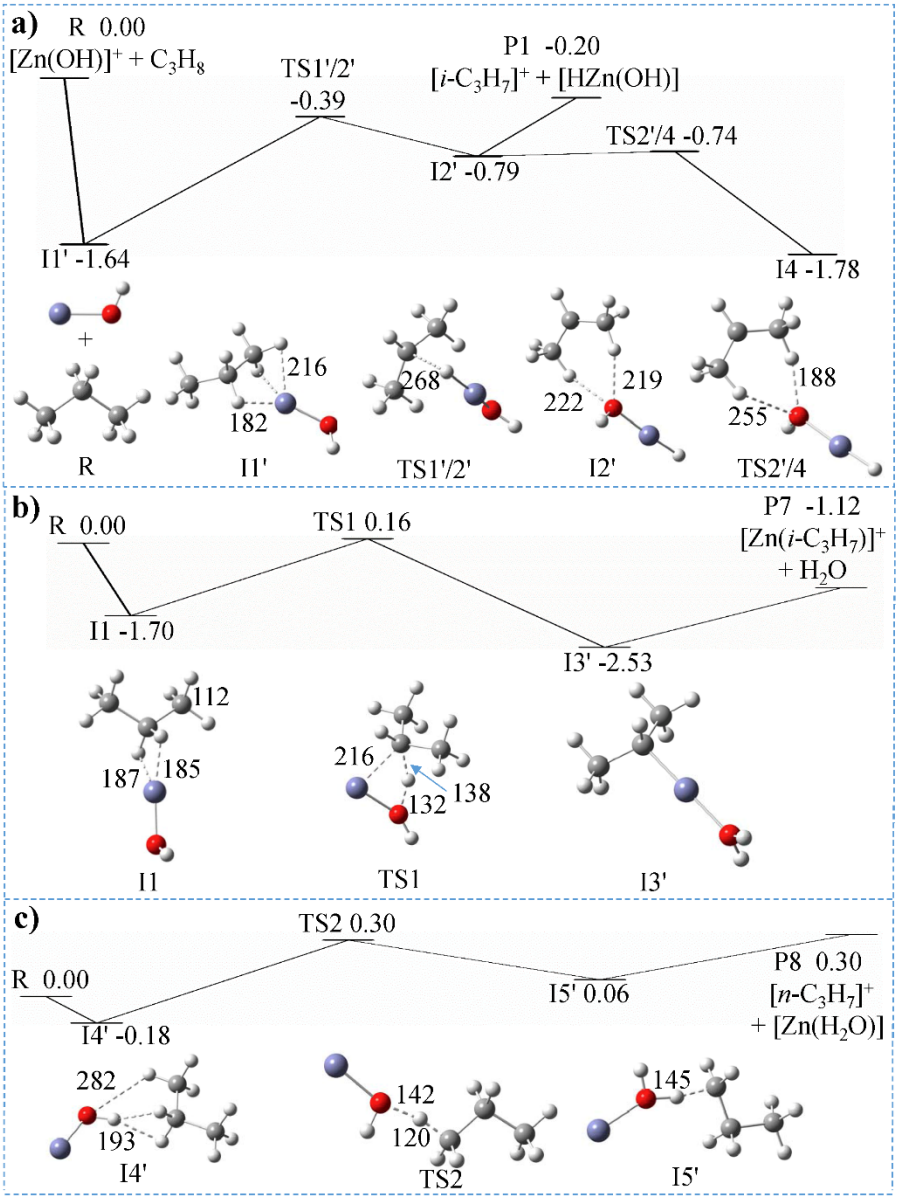

Figure S1: MP2-calculated additional possible potential-energy profiles for the reactions of $[Zn(OH)]^+$ with C_3H_8. The energies of intermediates and transition states are given relative to $[Zn(OH)]^+/C_3H_8$ (R): Color code: blue Zn, red O, gray C, and white H. Selected bond lengths are given in pm; relative ΔH_{0K} energies (in eV) are given with reference to the separated reactant pair.

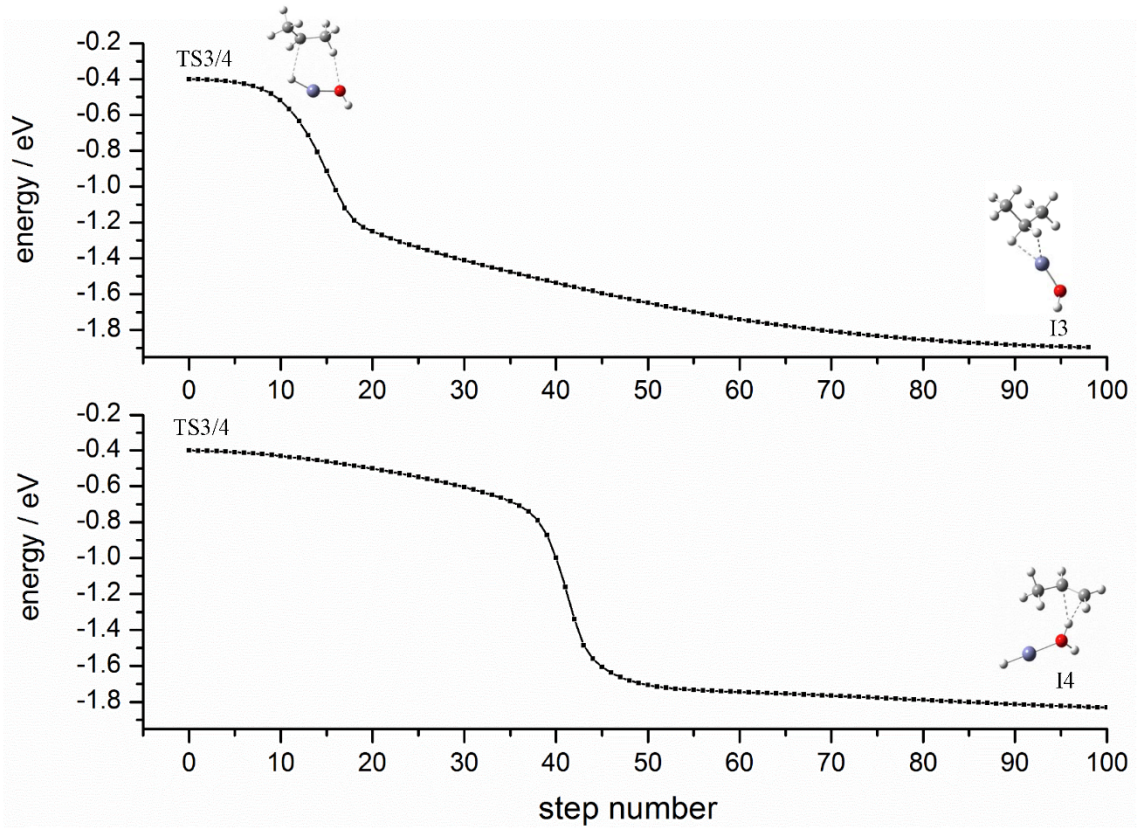

Figure S2: Intrinsic reaction coordinate (IRC) routes for TS3/4 in Figure 2.

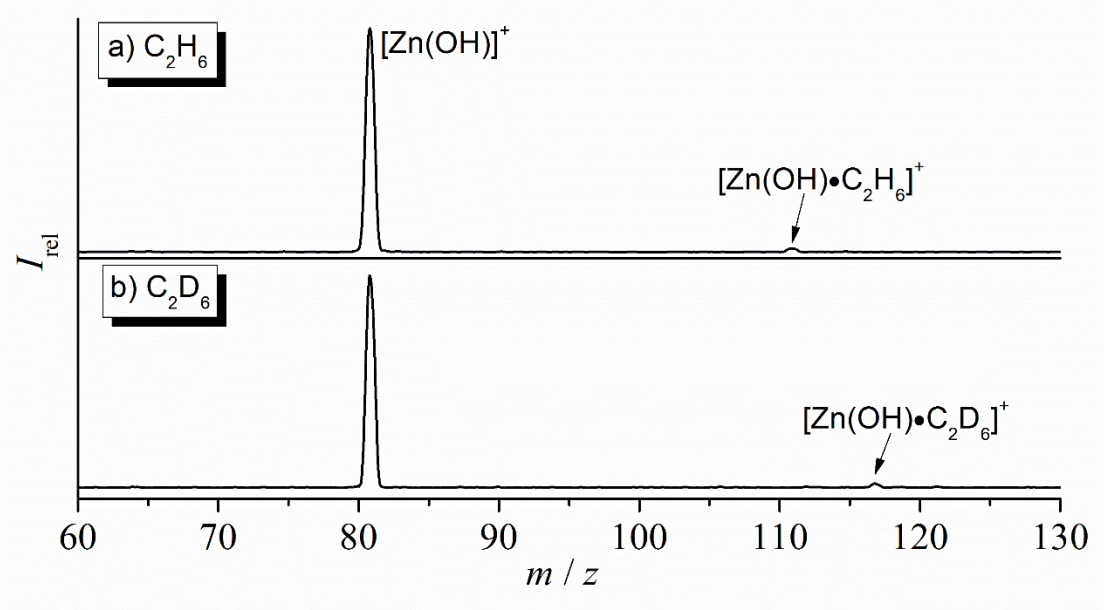

Figure S3: Mass spectra showing the ion/molecule reactions of mass-selected $[^{64}Zn(OH)]^+$ with C_2H_6 (a) and C_2D_6 (b) at a pressure of 1.0×10^{-3} mbar in the VG BIO-Q mass spectrometer.

Method	VDE ($[ZnOH]^-$)[a]	r_e(Zn-OH)[b]	Bond angle[c]	$D_0([ZnO]^+)$[d]	IE(ZnO)[e]
Experiment	1.78	1.809	114.2	1.65	9.34
MP2/6-311++G(2d,2p)	1.42	1.808	114.3	1.32	9.51

Table S1: Comparison of calculated results and experimental Data.

[a]VDE($[ZnOH]^-$) (in eV) represents the vertical detachment energy of ($[ZnOH]^-$), whose experimental value is taken from ref.1.

[b]r_e(ZnOH) (in Å) represents the bond length of Zn-OH; the experimental value is taken from ref.2.

[c]θ represents the bond angle in neutral ZnOH; the experimental value is taken from ref.2.

[d]$D_0([ZnO]^+)$ (in eV) represents the dissociation energy of $[ZnO]^+$; the experimental value is taken from the ref.3.

[e]IE(ZnO) (in eV) represents the ionization energies of ZnO, and the experimental value is taken from the ref.3.

Reference:

1. I. Iordanov, K. D. D. Gunaratne, C. L. Harmon, J. O. Sofo and A. W. Castleman, *J. Chem. Phys.*, 2012, 136.
2. L. N. Zack, M. Sun, M. P. Bucchino, D. J. Clouthier and L. M. Ziurys, *J. Phys. Chem. A*, 2012, 116, 1542.
3. D. E. Clemmer, N. F. Dalleska and P. B. Armentrout, *J. Chem. Phys.*, 1991, 95, 7263.

Method	TS3/4	P1	Δ(P1-TS3/4)
HF	-0.46	-0.38	0.06
PBE1PBE	-0.68	-0.56	0.12
BLYP	-0.91	-0.83	0.12
TPSS	-0.79	-0.64	0.15
BB95	-0.88	-0.77	0.11
B3LYP	-0.78	-0.71	0.07
BHANDHLYP	-0.68	-0.56	0.12
B2PLYP	-0.65	-0.51	0.14
M06	-0.98	-0.75	0.23
mPW2PLYP	-0.67	-0.51	0.15
MP2	-0.40	-0.20	0.20
CCSD(T)-cc-pVTZ	-0.38	-0.13	0.25

Table S2. The relative energies (in eV) of TS3/4 and P1 (relative to separated $[Zn(OH)]^+/C_3H_8$) obtained by various methods: HF→DFT→MP2→CCSD(T).

X	Low spin	X	High spin
$^1[Zn(OH)]^+ + {}^1C_3H_8$	0.0	$^3[Zn(OH)]^+ + {}^1C_3H_8$	1.77
$^1[i\text{-}C_3H_7]^+ + {}^1[HZn(OH)]$	-0.20	$^1[i\text{-}C_3H_7]^+ + {}^3[HZn(OH)]$	3.00
$^1[i\text{-}C_3H_7]^+ + {}^1[Zn(H_2O)]$	0.06	$^1[i\text{-}C_3H_7]^+ + {}^3[Zn(H_2O)]$	3.83
$^1[HZn(H_2O)]^+ + {}^1C_3H_6$	-1.12	$^3[HZn(H_2O)]^+ + {}^1C_3H_6$	1.63
$^1[Zn(i\text{-}C_3H_7)]^+ + {}^1H_2O$	-1.12	$^3[Zn(i\text{-}C_3H_7)]^+ + {}^1H_2O$	0.69
$^1[n\text{-}C_3H_7]^+ + {}^1[HZn(OH)]$	0.06	$^1[n\text{-}C_3H_7]^+ + {}^3[HZn(OH)]$	3.26
$^1[n\text{-}C_3H_7]^+ + {}^1[Zn(H_2O)]$	0.33	$^1[n\text{-}C_3H_7]^+ + {}^3[Zn(H_2O)]$	4.10
$^1[Zn(n\text{-}C_3H_7)]^+ + {}^1H_2O$	-1.07	$^3[Zn(n\text{-}C_3H_7)]^+ + {}^1H_2O$	0.92

Table S3. MP2/6-311++G(2d,2p) calculated energies (in eV) of high-spin and low-spin products with respect to the ground state $^1[Zn(OH)]^+/ {}^1C_3H_8$ in the reaction of $[Zn(OH)]^+$ with C_3H_8.

X	Low spin	X	High spin
$^1[Zn(OH)]^+ + {}^1C_2H_6$	0.0	$^3[Zn(OH)]^+ + {}^1C_2H_6$	1.77
$^1[C_2H_5]^+ + {}^1[HZn(OH)]$	0.58	$^1[C_2H_5]^+ + {}^3[HZn(OH)]$	3.77
$^1[C_2H_5]^+ + {}^1[Zn(H_2O)]$	0.84	$^1[C_2H_5]^+ + {}^3[Zn(H_2O)]$	4.61
$^1[Zn(H_2O)]^+ + {}^2C_2H_5$	0.41	$^3[Zn(H_2O)]^+ + {}^2CH_3$	9.15

Table S4. MP2/6-311++G(2d,2p) calculated energies (in eV) of high-spin and low-spin products with respect to the ground state $^1[ZnOH]^+/ {}^1C_2H_6$ in the reaction of $[Zn(OH)]^+$ with C_2H_6.

X	Low spin	X	High spin
$^1[Zn(OH)]^+ + {}^1CH_4$	0.0	$^3[Zn(OH)]^+ + {}^1CH_4$	1.77
$^1[CH_3]^+ + {}^1[HZn(OH)]$	2.39	$^1[CH_3]^+ + {}^3[HZn(OH)]$	5.59
$^1[CH_3]^+ + {}^1[Zn(H_2O)]$	2.65	$^1[CH_3]^+ + {}^3[Zn(H_2O)]$	6.42
$^1[Zn(H_2O)]^+ + {}^2CH_3$	0.53	$^3[Zn(H_2O)]^+ + {}^2CH_3$	9.25

Table S5. MP2/6-311++G(2d,2p) calculated energies (in eV) of high-spin and low-spin products with respect to the ground state $^1[ZnOH]^+/^1CH_4$ in the reaction of $[Zn(OH)]^+$ with CH_4.