Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information of "Carboranes: The Strongest Brønsted Acids in Alcohol Dehydration"

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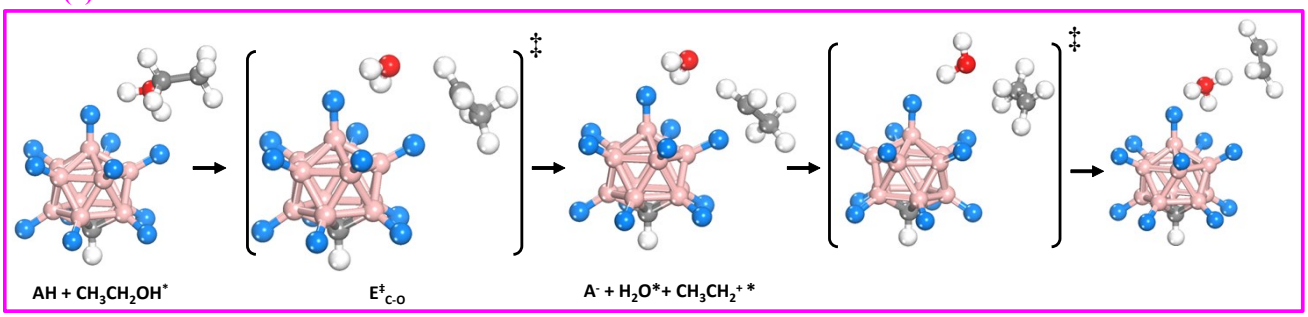
S1: Benchmark comparison of the effect of diffuse functions added to the basis set on the initial elementary steps of ethanol dehydration catalyzed by F-Carb, via the sequential mechanism (BE and $E^{\ddagger}_{C\text{-}O}$ are compared) The addition of diffuse functions has a minor effect on converged geometries and associated energies.

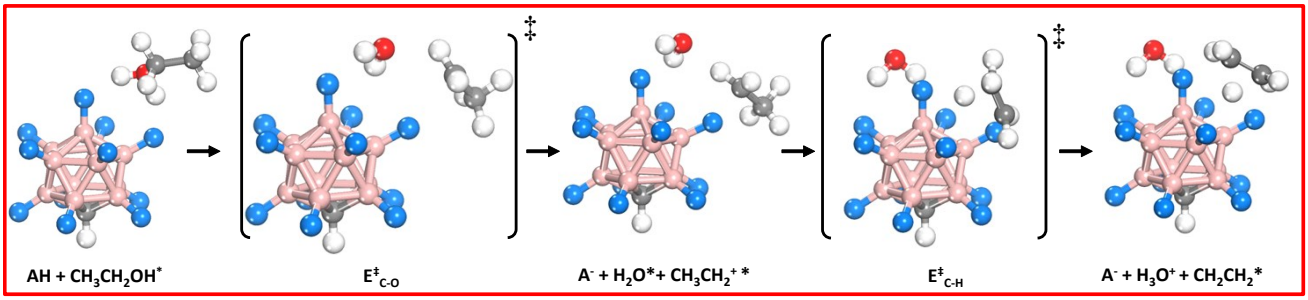
Level of Theory	$E^{\ddagger}_{C\text{-}O}$	BE
B3LYP/6-311G*	162.3	-248.3
B3LYP/6-311+G*	154.8	-237.9

S2: Graphical snapshots of competing pathways reported in Figures 1 and 4 of the manuscript. Representations of the sequential (E1 – a,b) and intramolecular (c,d) mechanisms are reported according to reaction coordinates reported in Figure 1 and the color scheme used in Figure 4. Adsorbed species are denoted with an asterisk (*) and the transition states denoted with a double dagger (‡).

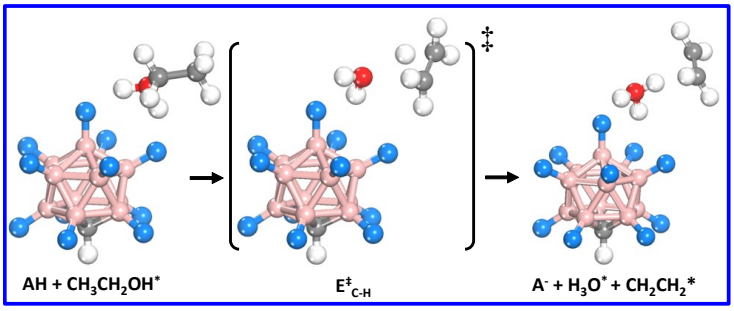
Path (a)



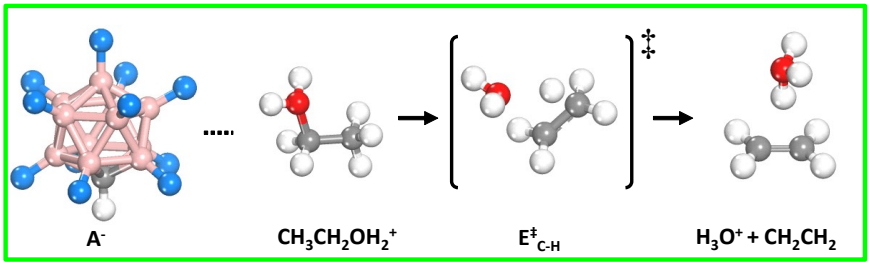
Path (b)



Path (c)



Path (d)



S3: Ethanol dehydration energy barriers calculated for the case of conjugate base anion dissociation in terms of electronic (E_a) and free energies (G_a). Cycle 1 refers to an H^+ catalyst, whereas Cycle 2 refers to H_3O^+ as the proton donor. Included are cases of solvation by continuum solvent shells of water, ethanol, 1-propanol, 2-propanol and t-butanol. Values are reported in kJ/mol.

	Cycle 1		Cycle 2	
Solvent	E_a (kJ/mol)	G_a (kJ/mol)	E_a (kJ/mol)	G_a (kJ/mol)
Water	135.0	109.1	176.6	153.7
Ethanol	134.1	107.3	176.1	148.6
1-Propanol	133.8	106.6	175.9	151.1
2-Propanol	133.7	106.7	175.0	148.2
t-Butanol	132.8	105.6	174.3	147.9

S4: Calculated gas-phase natural bond orbital (NBO) partial charges in the transition states for the complete set of alcohols and acids at the B3LYP/6-311G* level of theory. The columns in the table correspond to the partial charge of the carborane anion (A^-), water leaving group (H_2O) and the carbenium ion (CI).

	Reacting Alcohol	A^-	H_2O	CI
F-Carb	ethanol	-0.933	0.040	0.893
	1-propanol	-0.934	0.066	0.868
	2-propanol	-0.956	0.034	0.922
	t-butanol	-0.957	0.021	0.936
Cl-Carb	ethanol	-0.919	0.053	0.866
	1-propanol	-0.900	0.067	0.833
	2-propanol	-0.952	0.041	0.911
	t-butanol	-0.951	0.027	0.924
Br-Carb	ethanol	-0.879	0.046	0.833
	1-propanol	-0.844	0.051	0.793
	2-propanol	-0.933	0.033	0.900
	t-butanol	-0.919	0.013	0.906

S5: Calculated NBO partial charges in the transition states for the complete set of alcohols and acids in the presence of all solvents at the B3LYP/6-311G* level of theory. The columns in the table correspond to the partial charge of the carborane anion (A^-), water leaving group (H_2O) and the carbenium ion (CI). Cells containing "N/A" correspond to t-butanol transition states we were unable to locate due to additional stabilization by solvation, as described in the manuscript text.

	Reacting Alcohol	Solvent System	A^-	H_2O	CI
F-Carb	ethanol	H_2O	-0.947	0.038	0.913
	1-propanol		-0.953	0.061	0.888
	2-propanol		-0.969	0.030	0.941
	t-butanol		-0.983	0.015	0.965
	ethanol	ethanol	-0.978	0.071	0.906
	1-propanol	1-propanol	-0.951	0.061	0.886
	2-propanol	2-propanol	-0.980	0.036	0.942
	t-butanol	t-butanol	-0.981	0.018	0.963
Cl-Carb	ethanol	H_2O	-0.992	0.073	0.92
	1-propanol		-0.999	0.086	0.910
	2-propanol		-0.998	0.047	0.951
	t-butanol		N/A	N/A	N/A
	ethanol	ethanol	-0.95	0.051	0.900
	1-propanol	1-propanol	-0.934	0.062	0.872
	2-propanol	2-propanol	-1.006	0.051	0.952
	t-butanol	t-butanol	N/A	N/A	N/A
Br-Carb	ethanol	H_2O	-0.989	0.073	0.915
	1-propanol		-0.992	0.08	0.915
	2-propanol		-0.966	0.036	0.929
	t-butanol		N/A	N/A	N/A
	ethanol	ethanol	-0.989	0.075	0.915
	1-propanol	1-propanol	-0.989	0.076	0.913
	2-propanol	2-propanol	-0.992	0.045	0.946
	t-butanol	t-butanol	-0.994	0.019	0.975

S6: Calculated gas-phase NBO partial charges in the transition states for the complete set of alcohols and acids at the B3LYP/6-311G* level of theory in the presence of one additional explicit water molecule. The columns in the table correspond to the partial charge of the carborane anion (A^-), water dimer ($2 \cdot H_2O$) and the carbenium ion (CI).

	Reacting Alcohol	A^-	$2 \cdot H_2O$	CI
F-Carb	ethanol	-0.965	0.121	0.844
	1-propanol	-0.964	0.111	0.853
	2-propanol	-0.965	0.071	0.894
	t-butanol	-0.960	0.037	0.923
Cl-Carb	ethanol	-0.970	0.119	0.851
	1-propanol	-1.017	0.156	0.861
	2-propanol	-0.978	0.080	0.898
	t-butanol	-0.978	0.051	0.927
Br-Carb	ethanol	-0.944	0.107	0.837
	1-propanol	-0.948	0.097	0.851
	2-propanol	-0.956	0.071	0.885
	t-butanol	-0.953	0.041	0.912

S7: Calculated NBO partial charges in the transition states for the complete set of alcohols and acids at the B3LYP/6-311G* level of theory in the presence of a water solvation shell and one additional explicit water molecule. The columns in the table correspond to the partial charge of the carborane anion (A^-), water dimer ($2 \cdot H_2O$) and the carbenium ion (CI). Cells containing "N/A" correspond to t-butanol transition states we were unable to locate due to additional stabilization by solvation, as described in the manuscript text.

	Reacting Alcohol	A^-	$2 \cdot H_2O$	CI
F-Carb	ethanol	-0.984	0.049	0.892
	1-propanol	-0.983	0.051	0.891
	2-propanol	-0.983	0.010	0.937
	t-butanol	N/A	N/A	N/A
Cl-Carb	ethanol	-1.003	0.063	0.888
	1-propanol	-0.999	0.050	0.894
	2-propanol	-1.003	0.030	0.930
	t-butanol	-1.002	0.013	0.948
Br-Carb	ethanol	-0.995	0.059	0.887
	1-propanol	-0.995	0.057	0.891
	2-propanol	-0.996	0.028	0.928
	t-butanol	N/A	N/A	N/A

S8: Calculated activation free energies at 298 K in the presence of solvent shells (IWS, IAS) of protonated ethanol, 1-Propanol and 2-Propanol dissociated from carborane anion (A-) via the concerted intramolecular elimination mechanism in the presence of IWS and IAS. Values are reported in kJ/mol.

	Cycle 1	Cycle 2
Species	G_a (kJ/mol)	G_a (kJ/mol)
Ethanol (IWS)	109.1	153.7
Ethanol (IAS)	107.3	148.6
1-Propanol (IWS)	89.7	135.8
1-Propanol (IAS)	95.2	138.1
2-Propanol (IWS)	59.4	102.5
2-Propanol (IAS)	60.4	103.7

S9: Calculated activation free energies at 298 K in the gas phase (GP) and in the presence of solvent shells (IWS, IAS) for all acid-alcohol combinations. Values reported in kJ/mol.

	Species	GP	IWS	IAS
F-carb	ethanol	151.9	119.0	120.0
	1-propanol	129.2	113.1	114.7
	2-propanol	102.0	70.5	68.1
	t-butanol	63.9	38.8	39.1
Cl-carb	ethanol	148.3	107.5	107.7
	1-propanol	129.3	91.9	94.1
	2-propanol	107.1	62.8	60.0
	t-butanol	61.5	37.6	35.6
Br-carb	ethanol	155.5	109.8	109.8
	1-propanol	130.9	99.9	102.3
	2-propanol	118.9	59.2	63.8
	t-butanol	71.2	40.1	40.5

S10: Selected geometry configurations of ethanol dehydration on F-Carb superacid under IWS. Included are converged ground and transition states for the concerted and sequential pathways.

Ground state configuration of F-Carb superacid (AH):

B	-0.10199100	-0.10896900	-0.02753600
B	-0.05843400	-0.13840500	1.83483600
B	1.70018100	-0.04666300	2.35668500
B	2.70579200	0.04995800	0.84017400
B	1.63007600	0.00161100	-0.62911600
B	0.87367600	-1.59505700	2.32954800
B	2.59257800	-1.45587300	1.73733400
B	2.54967300	-1.42681800	-0.09752600
B	0.80495900	-1.54789600	-0.61185700
B	-0.21755200	-1.63725600	0.88300600
B	1.11649700	0.76012400	0.88957500
C	1.38472100	-2.28431300	0.83432500
F	3.56528500	-2.14804000	2.36205100
F	3.49170000	-2.09774400	-0.78901100
F	0.47975100	-2.32026800	-1.66820900
F	0.59962000	-2.40107900	3.37495700
F	-1.27158700	-2.47899500	0.89364800
F	3.64987300	1.09950400	0.83455700
F	1.96100600	0.77219400	-1.70167800
F	-1.13053500	0.45476000	-0.70419000
F	2.08299200	0.68959700	3.43623300
F	-1.05345800	0.40352000	2.57619000
F	1.45364300	2.29503600	0.90644200
H	1.46430200	-3.36682600	0.81497100
H	2.43727600	2.29587000	0.88345100

Ground state configuration of ethanol protonated by F-Carb (AH + $CH_3CH_2OH^*$)

B	0.12596700	0.18066300	0.07157700
B	-0.26314400	-0.25856500	1.79140300
B	1.29448400	-0.62792700	2.64274400
B	2.63384600	-0.41896000	1.44640200
B	1.92537400	0.08486800	-0.14055800
B	0.25733200	-1.94099500	2.05762200
B	2.04073900	-2.03563700	1.85193000
B	2.42746400	-1.59774600	0.14343600
B	0.88076600	-1.23610200	-0.69689100
B	-0.45759700	-1.44687800	0.48407800
B	1.21677100	0.66872600	1.40235900
C	0.96996300	-2.39788200	0.56381600
F	2.74124500	-3.02855600	2.46076100
F	3.41284500	-2.26810500	-0.50981800
F	0.70718100	-1.64095900	-1.98372000
F	-0.37949800	-2.86970600	2.82010800
F	-1.62614100	-2.01076900	0.07597900
F	3.88346700	0.05917800	1.85108100
F	2.59766600	0.92429300	-0.99002800
F	-0.63139900	1.08478700	-0.62682200
F	1.47924000	-0.33889500	3.97205000
F	-1.32721500	0.29789100	2.45233200
F	1.36409500	2.01001500	1.77698400
H	0.88225000	-3.44073300	0.27685200
H	4.11127300	1.68146400	2.52978500

H	2.87288000	2.65361200	2.42594400
O	3.77385300	2.56223700	2.81517200
C	3.76282200	2.72516800	4.32726000
H	3.13331500	1.92528000	4.70992300
C	5.18199000	2.68467000	4.81922500
H	3.28448500	3.69083600	4.46057500
H	5.78308300	3.47107500	4.36169200
H	5.64964300	1.71471200	4.64020700
H	5.16568100	2.85007600	5.89905400

E1 Transition state of ethanol dissociation into ethyl carbocation and H_2O over F-Carb ($E^{\ddagger}_{C\text{-}O}$)

B	0.03858700	-0.29835100	-0.40148400
B	-0.59475500	-0.05370200	1.27881500
B	0.78562700	0.48302600	2.31567400
B	2.26726300	0.57316100	1.28608800
B	1.80758500	0.09215300	-0.39696500
B	0.23742200	-1.20423000	2.34947400
B	1.99249500	-0.81706500	2.35636100
B	2.61838700	-1.05960100	0.68960100
B	1.25249500	-1.59465200	-0.34443500
B	-0.21887700	-1.68370100	0.68156400
B	0.66580600	1.04013700	0.61518400
C	1.34058200	-2.01426600	1.31765600
F	2.75598200	-1.17674000	3.42383700
F	3.85338900	-1.60349000	0.51123700
F	1.46450900	-2.54394400	-1.29685200
F	-0.30744700	-1.85406400	3.41399600
F	-1.10554800	-2.69971000	0.49441700
F	3.26666900	1.49755000	1.52347900
F	2.42999200	0.63357000	-1.49369200
F	-0.74503100	-0.06859000	-1.50468700
F	0.58373400	1.33342300	3.39087600
F	-1.87752200	0.37472100	1.51155600
F	0.37173600	2.35896100	0.31357000
H	1.56664800	-3.04909700	1.55284400
H	2.67440500	3.40699700	1.98645100
H	1.27037800	3.74378000	1.46284900
O	1.91851100	3.98960500	2.13631700
C	1.00769600	3.46170900	4.72541800
H	-0.05048700	3.22797000	4.78381300
C	1.93058800	2.84523200	5.60324500
H	1.31476400	4.25280900	4.04864800
H	2.97834900	2.91912100	5.31862800
H	1.62545100	1.89933300	6.04335300
H	1.79867400	3.61727900	6.42042600

Ground state configuration of ethanol dissociated into carbocation and H_2O ($A^- + CH_2CH_3^+ + H_2O^*$)

B	0.05462100	0.02753000	0.08516700
B	-0.01848100	-0.00196100	1.89558200
B	1.68048200	0.01358700	2.49178600
B	2.80891700	0.07429800	1.09318500
B	1.79772700	0.07775000	-0.40856500
B	0.77334700	-1.50401600	2.44578200
B	2.50890500	-1.45497000	1.95504500
B	2.57247900	-1.42048700	0.16324200
B	0.88636700	-1.44785700	-0.45435500

B	-0.22504700	-1.49771000	0.95807000
B	1.24119300	0.97025800	1.04862500
C	1.32337800	-2.24434200	1.00385200
F	3.42166100	-2.16931000	2.66256200
F	3.54074800	-2.12094300	-0.48397300
F	0.59190000	-2.17706300	-1.56283700
F	0.41038600	-2.25636700	3.51626700
F	-1.34772000	-2.26169400	0.90145700
F	4.02597900	0.71618400	1.14602400
F	2.20701700	0.73083200	-1.54149700
F	-0.91907500	0.64019700	-0.65955500
F	1.95672200	0.60059100	3.76032500
F	-1.03657500	0.58718500	2.59516600
F	1.19838200	2.34857200	1.06836700
H	1.34847500	-3.32898500	0.98492600
H	4.21403200	2.84262400	1.49130900
H	2.83967900	3.51659600	1.59620000
O	3.71105800	3.48160400	2.01147000
C	3.19742800	1.83963200	4.57388200
H	2.40247000	2.17661700	5.22922700
C	4.23660300	0.99134500	5.10793700
H	3.36566300	2.42423000	3.66451800
H	4.87060800	0.53094400	4.35234000
H	3.89764400	0.29505400	5.87307100
H	4.86581300	1.74623400	5.62835500

Transition state of concerted intramolecular dehydration ($E^{\ddagger}_{C\text{-}H}$)

B	-0.04409200	0.15964400	-0.01198600
B	-0.03243400	-0.22542500	1.75910300
B	1.67888100	-0.55614100	2.24636900
B	2.72028400	-0.37618900	0.77855400
B	1.66057100	0.06874300	-0.61787500
B	0.55054400	-1.89415900	1.95024700
B	2.24151400	-1.98396800	1.35222300
B	2.23010800	-1.60153800	-0.40460900
B	0.53225200	-1.27565200	-0.88875400
B	-0.50421800	-1.45579700	0.56652300
B	1.31239900	0.71012600	1.02410700
C	0.91309200	-2.39870000	0.35122300
F	3.07160600	-2.95503200	1.82305300
F	3.05252600	-2.28814500	-1.24473300
F	0.07969500	-1.72031600	-2.09373600
F	0.11631600	-2.80067800	2.86902100
F	-1.73078100	-2.03578200	0.44785000
F	4.02444700	0.08253400	0.86936100
F	2.10977600	0.87690800	-1.63274200
F	-0.95191200	1.03751100	-0.55101800
F	2.14324600	-0.24975600	3.50681300
F	-0.92970500	0.34689700	2.62649300
F	1.48790500	2.05398100	1.30730800
H	0.77554000	-3.45060500	0.12400100
H	4.37524500	1.67861000	1.98535900
H	3.27910100	2.76009000	2.10746900
O	4.07338100	2.41448700	2.53645000
C	3.79508000	1.96402100	5.03654200
H	2.80656100	2.39865300	4.94157100

C	4.88348300	2.73918100	5.40012200
H	3.90208000	0.92510400	4.75016500
H	5.83501500	2.25961300	5.60148100
H	4.71911700	3.73486400	5.79713500
H	4.81989000	2.85329900	4.21223300

Ground state configuration of final dehydration products: H_2O and ethylene ($AH + C_2H_4^* + H_2O^*$)

B	0.01515500	0.04438900	0.04682100
B	0.05112000	0.01017300	1.86409800
B	1.78487500	-0.04614800	2.39178800
B	2.80795200	-0.05131400	0.89959000
B	1.72790000	0.00995400	-0.55108000
B	0.80285700	-1.52343000	2.36713800
B	2.50172900	-1.55415300	1.78045100
B	2.46646600	-1.52015100	-0.02427500
B	0.74648700	-1.46851400	-0.54228300
B	-0.27971800	-1.46701500	0.93339800
B	1.29947500	0.90271400	0.94587700
C	1.23105800	-2.28311400	0.88881200
F	3.42375800	-2.32546200	2.41464300
F	3.36177200	-2.26721600	-0.72256600
F	0.35191800	-2.18192000	-1.63084300
F	0.45082000	-2.27700400	3.44309900
F	-1.43681300	-2.18200700	0.94255000
F	4.05371800	0.58278800	0.88972000
F	2.10510900	0.65820600	-1.69785600
F	-0.96955100	0.70670300	-0.63878400
F	2.20950200	0.56405900	3.54429800
F	-0.90470400	0.64632700	2.61264100
F	1.35940700	2.30284500	0.96954100
H	1.20389200	-3.36773900	0.86891600
H	4.21989900	2.33198300	1.10601100
H	2.84884800	3.14448600	1.09398800
O	3.82823000	3.23168300	1.19966100
C	4.04365300	4.04504400	4.15552100
H	2.98616600	4.24264200	4.30113900
C	4.84716500	4.93011500	3.55882400
H	4.41882500	3.10020100	4.53632100
H	5.90848800	4.74059000	3.43158300
H	4.47517800	5.88292500	3.19525700
H	4.05582700	3.63858300	2.08926300