Electronic Supplementary Information (ESI)

New Insights in the Chemistry of Ionic Alkylorganic Carbonates: A Computational Study

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Computational Details:

All calculations were performed with Gaussian 09.[1] Geometry optimization and frequency calculations were carried out with B3LYP density functional with 6-31+G* basis set. Different starting geometries were considered, however, the most stable ones were considered for further calculations and free energy determination calculations. Minima were characterized by the absence of imaginary frequencies. A polarizable continuum model (PCM)[2] was used for implicit solvent calculations. pK_a calculations were performed in MeCN as follows:

$$HA_{(s)} \rightarrow A^-_{(s)} + H^+_{(s)}$$

$$\Delta G_{(s)} = G_{(s)}(A^-) + G_{(s)}(H^+) - G_{(s)}(HA)$$

$$pK_a = \frac{\Delta G_{(s)}}{2.303RT}$$

$G_{(s)}(H^+) = 255.2$ kcal mol^{-1} in MeCN was taken from Ref. [3].

Proton and carbon chemical shifts were computed using the gauge-independent atomic orbital (GIAO) method, in which tetramethylsilane was used as a reference.[4] The effect of solvation on the chemical shifts was studied by means of the self-consistent reaction-field (SRCF) method, based on the PCM implemented in Gaussian 09.[1]

Table S1. Calculated gas-phase proton affinity (PA in kcal mol^{-1})[a] of the studied bases and alcohols.

substrate	PA/ kcal mol^{-1}	substrate	PA/ kcal mol^{-1}
H_2O	382.97	BzOH	360.25
DBU	247.66	PF-MeOH	314.80
TMG	243.66	PF-EtOH	311.16
Bb	251.69	PF-PrOH	307.66
MeOH	373.20	PF-BuOH	307.17
EtOH	369.89	PF-*t*-BuOH	318.40
PrOH	369.54	PF-PentOH	306.57
i-PrOH	367.83	PF-HexOH	306.28
BuOH	369.04	PF-PhOH	317.82
t-BuOH	367.26	*p*-F-PhOH	337.25
PentOH	368.78	*p*-Cl-PhOH	333.82
HexOH	368.66	*p*-Cresol	341.17
CyHexOH	367.18	*p*-MeO-PhOH	342.70
CyHexMeOH	366.24	*p*-NO_2-PhOH	315.39
PhOH	340.55	PF-BuMeOH	346.45

[a] PA values were calculated using the Gaussian 09 software (B3LYP/6-31+G* level of theory) as the negative of the enthalpy change (ΔH) of the gas phase reaction, $A_{(g)} + H^+_{(g)} \rightarrow AH^+_{(g)}$. Under standard conditions, the value of the enthalpy of the gas-phase proton was taken as 1.48 kcal mol^{-1}.

Table S2. Free energy (kcal mol^{-1}) for the capture of CO_2 using different alcohol/base binary mixtures in gas phase (charges are omitted for clarity).

R(Ar)O-CO_2●countercation	$\Delta G_{capture}$	R(Ar)O-CO_2●countercation	$\Delta G_{capture}$
MeO-CO_2●Li	-49.73	PhO-CO_2●Li	-43.28
MeO-CO_2●Na	-41.87	PhO-CO_2●Na	-36.10
MeO-CO_2●K	-47.84	PhO-CO_2●K	-42.61
MeO-CO_2●DBUH	8.34	PhO-CO_2●DBUH	14.07
MeO-CO_2●TMGH	7.12	PhO-CO_2●TMGH	15.92
MeO-CO_2●BbH	8.80	PhO-CO_2●BbH	13.50
EtO-CO_2●Li	-48.88	BzO-CO_2●Li	-47.74
EtO CO_2●Na	-40.81	BzO-CO_2●Na	-40.06
EtO-CO_2●K	-46.70	BzO-CO_2●K	-46.08
EtO-CO_2●DBUH	9.25	BzO-CO_2●DBUH	10.62
EtO-CO_2●TMGH	8.32	BzO-CO_2●TMGH	9.76
EtO-CO_2●BbH	9.35	BzO-CO_2●BbH	10.07
PrO-CO_2●Li	-48.76	PF-MeO-CO_2●Li	60
PrO-CO_2●Na	-40.92	PF-MeO-CO_2●Na	-35.71
PrO-CO_2●K	-46.81	PF-MeO-CO_2●K	-43.99
PrO-CO_2●DBUH	9.27	PF-MeO-CO_2●DBUH	11.94
PrO-CO_2●TMGH	8.53	PF-MeO-CO_2●TMGH	14.28
PrO-CO_2●BbH	9.60	PF-MeO-CO_2●BbH	10.17
i- PrO-CO_2●Li	-45.44	PF-EtO-CO_2●Li	-40.33
i- PrO-CO_2●Na	-37.25	PF-EtO-CO_2●Na	-35.64
i- PrO-CO_2●K	-43.06	PF-EtO-CO_2●K	-44.12

i- PrO-CO_2●DBUH	13.30	PF-EtO-CO_2●DBUH	12.05
i- PrO-CO_2●TMGH	11.44	PF-EtO-CO_2●TMGH	16.83
i- PrO-CO_2●BbH	13.57	PF-EtO-CO_2●BbH	10.20
BuO-CO_2●Li	-48.81	PF-PrO-CO_2●Li	-39.99
BuO-CO_2●Na	-40.83	PF-PrO-CO_2●Na	-35.32
BuO-CO_2●K	-46.70	PF-PrO-CO_2●K	-43.93
BuO-CO_2●DBUH	9.43	PF-PrO-CO_2●DBUH	12.22
BuO-CO_2●TMGH	8.21	PF-PrO-CO_2●TMGH	16.61
BuO-CO_2●BbH	9.37	PF-PrO-CO_2●BbH	10.96
t-BuO-CO_2●Li	-44.78	PF-BuO-CO_2●Li	-40.25
t-BuO-CO_2●Na	-36.58	PF-BuO-CO_2●Na	-35.69
t-BuO-CO_2●K	-42.31	PF-BuO-CO_2●K	-44.16
t-BuO-CO_2●DBUH	14.03	PF-BuO-CO_2●DBUH	12.46
t-BuO-CO_2●TMGH	12.11	PF-BuO-CO_2●TMGH	13.60
t-BuO -CO_2●BbH	13.38	PF-BuO-CO_2●BbH	10.60
PentO-CO_2●Li	-48.94	PF-*t*-BuO-CO_2●Li	-38.61
PentO-CO_2●Na	-40.94	PF-*t*-BuO-CO_2●Na	-33.96
PentO-CO_2●K	-46.76	PF-*t*-BuO-CO_2●K	-42.20
PentO-CO_2●DBUH	9.48	PF-*t*-BuO-CO_2●DBUH	13.53
PentO-CO_2●TMGH	8.48	PF-*t*-BuO-CO_2●TMGH	16.83
PentO-CO_2●BbH	9.44	PF-*t*-BuO-CO_2●BbH	12.69
HexO-CO_2●Li	-48.66	PF-PentO-CO_2●Li	-40.31
HexO-CO_2●Na	-41.02	PF-PentO-CO_2●Na	-35.81
HexO-CO_2●K	-46.63	PF-PentO-CO_2●K	-44.27
HexO-CO_2●DBUH	9.58	PF-PentO-CO_2●DBUH	12.22
HexO-CO_2●TMGH	9.05	PF-PentO-CO_2●TMGH	14.50
HexO-CO_2●BbH	10.45	PF-PentO-CO_2●BbH	10.10
CyHexO-CO_2●Li	-48.30	PF-HexO-CO_2●Li	-40.35
CyHexO-CO_2●Na	-40.24	PF-HexO-CO_2●Na	-35.82
CyHexO-CO_2●K	-45.94	PF-HexO-CO_2●K	-44.32
CyHexO-CO_2●DBUH	10.89	PF-HexO-CO_2●DBUH	12.07
CyHexO-CO_2●TMGH	9.19	PF-HexO-CO_2●TMGH	14.47
CyHexO-CO_2●BbH	10.53	PF-HexO-CO_2●BbH	10.40
CyHexMeO-CO_2●Li	-49.35	PF-PhO-CO_2●Li	-44.49
CyHexMeO-CO_2●Na	-41.54	PF-PhO-CO_2●Na	-38.71
CyHexMeO-CO_2●K	-47.43	PF-PhO-CO_2●K	-44.74
CyHexMeO-CO_2●DBUH	10.72	PF-PhO-CO_2●DBUH	9.15
CyHexMeO-CO_2●TMGH	8.49	PF-PhO-CO_2●TMGH	11.76
CyHexMeO-CO_2●BbH	9.17	PF-PhO-CO_2●BbH	8.01

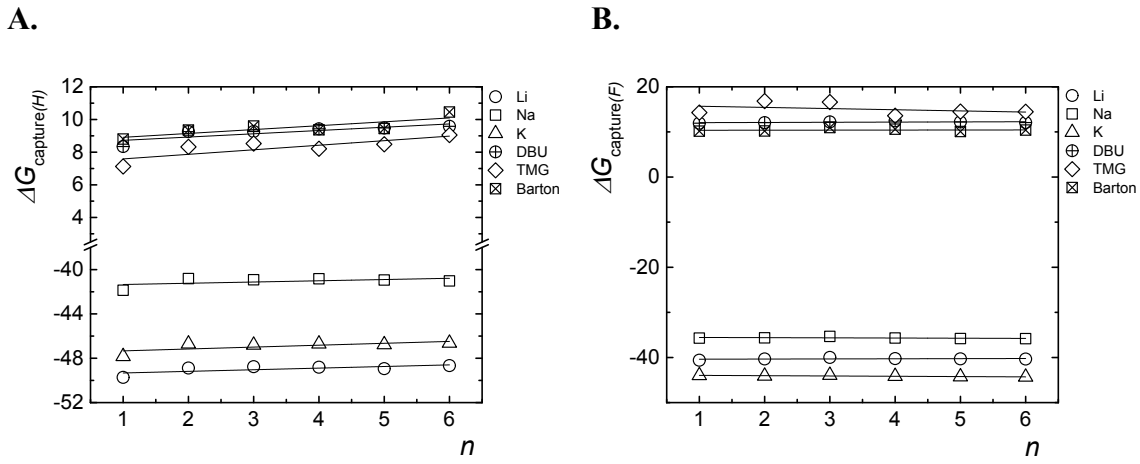

Figure S1. Free energy values for CO_2 capturing ($\Delta G_{capture}$) in gas phase for linear alcohols *versus* number of carbon atoms. **A**. Hydrogenated alcohols. **B**. PFAs.

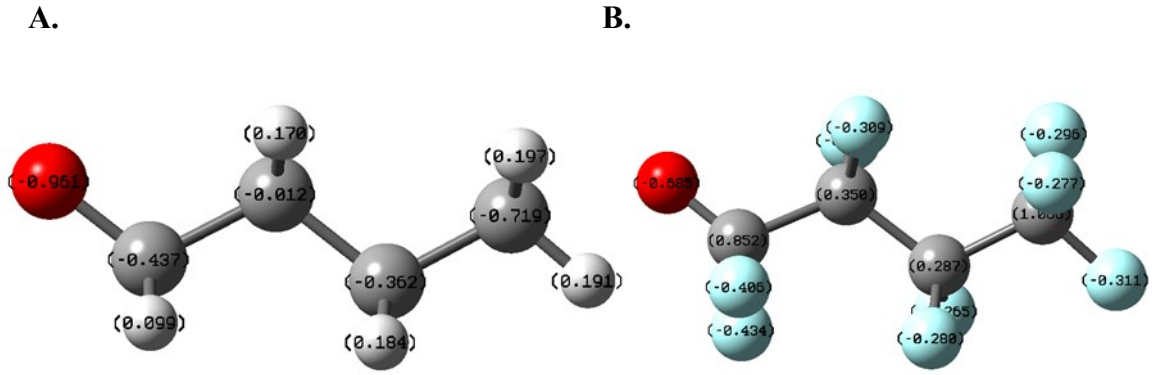

Figure S2. Mulliken charges on **A.** BuOH and **B.** PF-BuOH, calculated in MeCN.

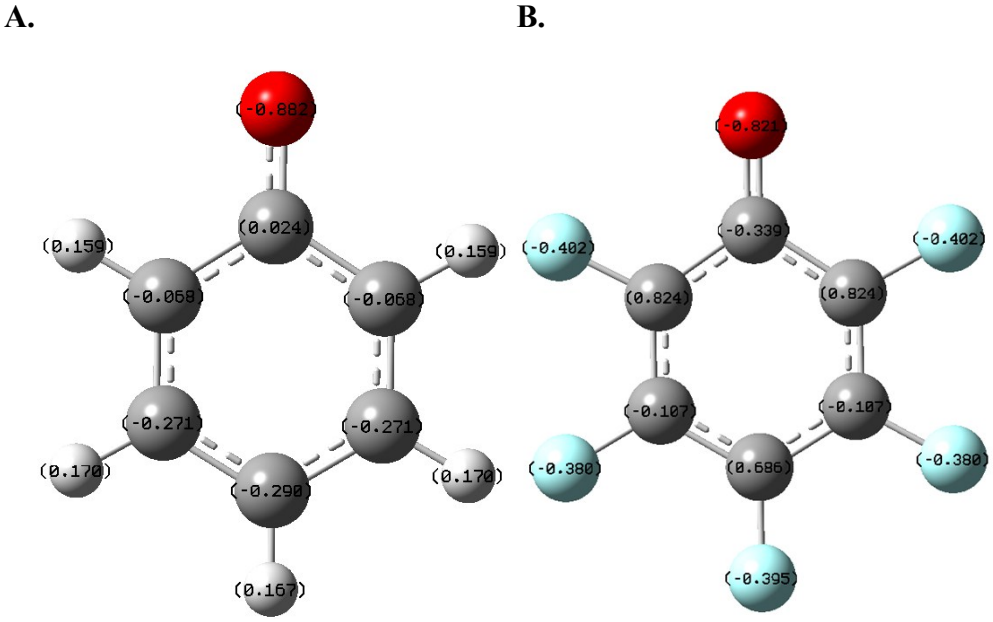

Figure S3. Mulliken charges on **A**. PhOH and **B**. PF-PhOH, calculated in MeCN.

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