Supporting Information for:

Entropic Corrections for the Evaluation of the Catalytic Activity in the Al(III) Catalysed Formation of Cyclic Carbonates from CO$_2$ and Epoxides

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1. Methods for evaluating entropies in solution

Ideal gas assumption is considered in order to obtain the different molecular partition functions. Hence, all the equations used in electronic-structure calculations are applicable to a hypothetical ideal gas at concentrations equivalent to standard state, where pressure $P =$ 1 atm. Because of this choice, we may replace V by RT/P and specify a standard state pressure instead, corresponding to a standard-state molar volume of 24.5 L at 298.15 K. Thus, a concentration of 1/24.5 M can be derived from the well-known expression:

$$\frac{n}{V} = \frac{P}{RT}$$

(eq. S1.0)

This logarithmic concentration is used to calculate the translational entropy contribution S_{trans} by means of the partition function:

$$q_{trans} = \left(\frac{2\pi mRT}{h^2}\right)^{3/2} \frac{RT}{P}$$

(eq. S1.1)

In real chemical processes where an ensemble of molecules are interacting each other or with the solvent medium, the ideal gas-phase translational entropy significantly overestimates the condensed-phase translational entropy, as a result of the restriction of motion of molecules in solution.[1] In addition, we do not have solutions whose concentration is 1/24.5 M, and therefore it is necessary to obtain results applicable at the concentration of the system under study. At this point it should be highlighted that accurate prediction of the translational entropy contribution S_{trans} to the total entropy in solution is still challenging in electronic-structure calculations, and so far no standard approach is available. However, many authors have proposed some methods for dealing with this issue, as discussed below.

The simplest of these approximations is maybe the one introduced by Morokuma and coworkers.[2] They suggest neglecting directly the translational entropy term in the calculation of the total entropy in solution.

Alternatively, Martin and coworkers[3] proposed to determine the pressure $P = \frac{n}{V}RT$ (from equation S1.0) applicable at the concentration of the solvent used from its experimental density. Thus, for example the liquid water, with a density ρ = 997.02 kg·m^{-3}, requires a pressure of 1354 atm to correct the aqueous solution concentration. The actual concentration (1354 atm/RT) is incorporated then to the calculation of the translational partition function in equation 1.1. By applying this approximation for the solvent 1,2-epoxyhexane (ρ = 831.0 kg·cm^{-3}) we obtained a pressure of 203 atm, which is used for adjusting the solvent concentration of the gas-phase entropies.

The third approximation employed in this study is the method of Wertz[4] and Ziegler,[5] which is broken up into three steps. In the first step based on this method, the ideal-gas solute is compressed from standard conditions (having a molar volume $V_{m,gas}$ of 24450 mL·mol^{-1}) to the standard volume of the solvent ($V_{m,liq}$). Then the compressed solute gas is transferred to the solvent, forming a hypothetical solution that has the intermolecular interactions of a dilute

solution. In this step the solute loses the same fraction of its entropy as would be lost by the solvent in going from gas (at its liquid-phase density) to liquid. This fraction α can be calculated by use of equation S1.2, in which the numerator represents the change in entropy in the process of transfer. In the third step, the solute is expanded to the concentration of the desired solution (i.e., 1.0 mol·L^{-1}, and thus having molar volume of V_m^o = 1000 mL·mol^{-1}).

The solute entropy change for the first and third steps, which are strictly changes in molar volume, is given by $\Delta S = R \ln \left(V_{m,f}/V_{m,i} \right)$, where $V_{m,f}$ is the final solute molar volume and $V_{m,i}$ is the initial solute value. The entropy fraction α lost in the second step can be determined from the absolute entropies of the solvent in its gas (S_{gas}^o) and liquid (S_{liq}^o) phases (see Table S1), as shown in equation S1.2:

$$\alpha = \frac{S_{liq}^o - \left(S_{gas}^o + R \ln V_{m,liq}/V_{m,gas} \right)}{S_{gas}^o + R \ln V_{m,liq}/V_{m,gas}}$$

(eq. S1.2)

Substituting the appropriate parameters for 1,2-epoxyhexane[6] in equation S1.2, we have $\alpha = -\,0.19$. The sum of the entropy changes involved in each of the three steps then gives the total solvation entropy. Using the data reported in Table S.1 we are able to calculate the entropy (cal·mol^{-1}·K^{-1}) of solvation for a given species of the reaction in 1,2-epoxyhexane ΔS_{sol}, at a temperature of 298.15 K:

$$\Delta S_{sol} = (-\,10.56 \text{ cal·mol}^{-1}\text{·K}^{-1}) - 0.19(S_{gas} - 10.56 \text{ cal·mol}^{-1}\text{·K}^{-1}) + (4.20 \text{ cal·mol}^{-1}\text{·K}^{-1})$$

(eq. S1.3)

Table S1 Experimental data[6] for the solvent 1,2-epoxyhexane used in equations S1.2 and S1.3.

| M^a (g·mol^{-1})	ρ^a (g·cm^{-3})	S_{liq}^o ^{b} (J·mol^{-1}·K^{-1})	S_{gas}^o ^{b} (kcal·mol^{-1})	$R \ln V_{m,liq}/V_{m,gas}$ (cal·mol^{-1}·K^{-1})	$R \ln V_m^o/V_{m,liq}$ (cal·mol^{-1}·K^{-1})
100.16	0.831	196.27	287.40	−10.56	4.20

^{a} These values were taken from the thermochemistry data for propylene oxide. ^{b} These values were considered for 1,2-epoxyhexane.

2. Relative Gibbs free-energies including entropic corrections. Geometry optimization in gas-phase
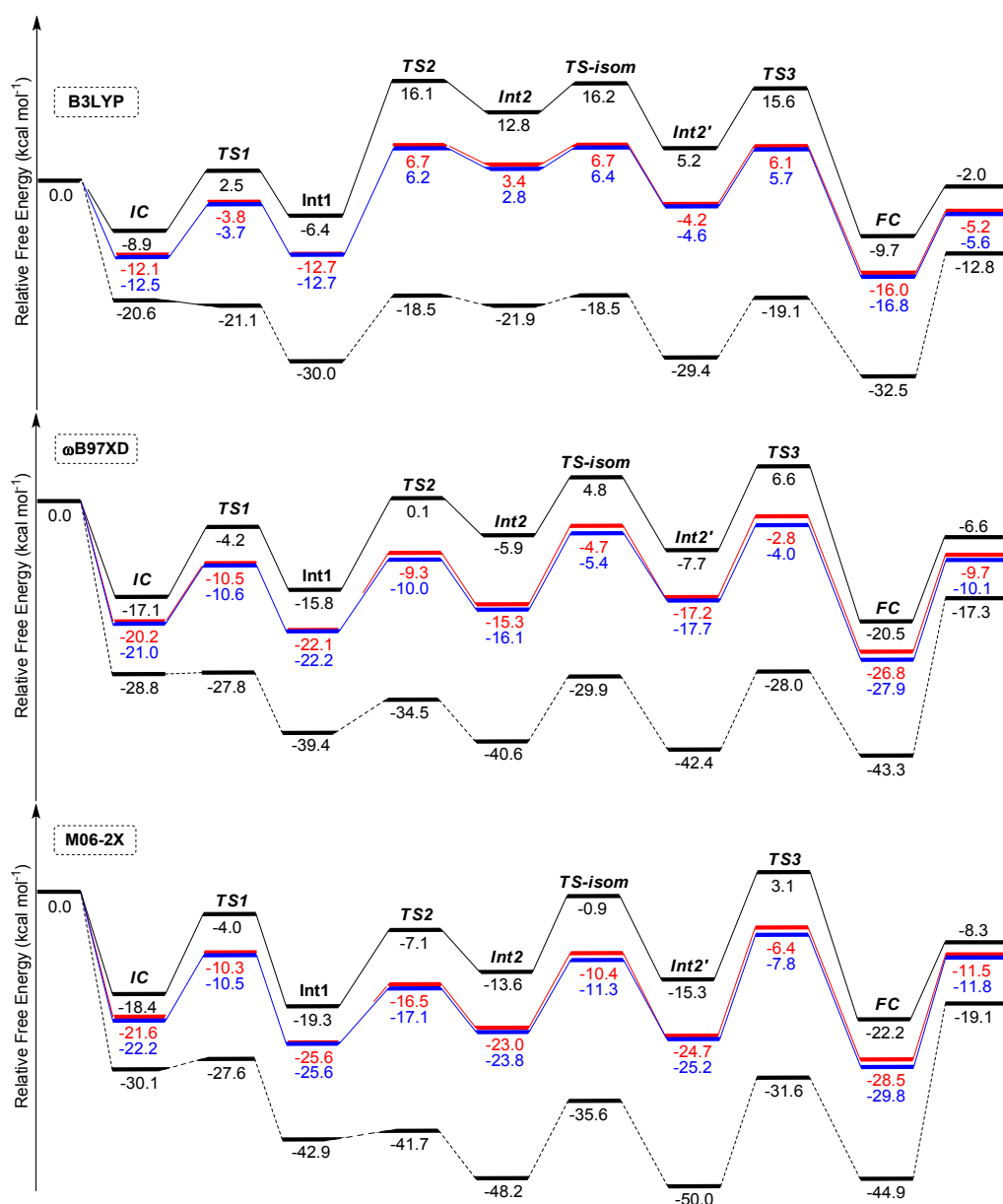
Figure S1. Free-energy profiles for cyclic carbonate formation from CO_2 and 1,2-epoxyhexane catalyzed by [Al{amino-tris(phenolate)}]/NBu$_4$I, calculated at different levels. The solid black line represents the pathway without considering any kind of corrections for entropy in solution, whereas the dashed black line stands for the pathway including only the vibrational and rotational terms in the calculation of the total entropy in solution. The pathways considering entropy corrections by Martin, and Wertz/Ziegler appear in red and blue, respectively.

3. Relative Gibbs free energies including entropic corrections. Geometry optimizations in solvent
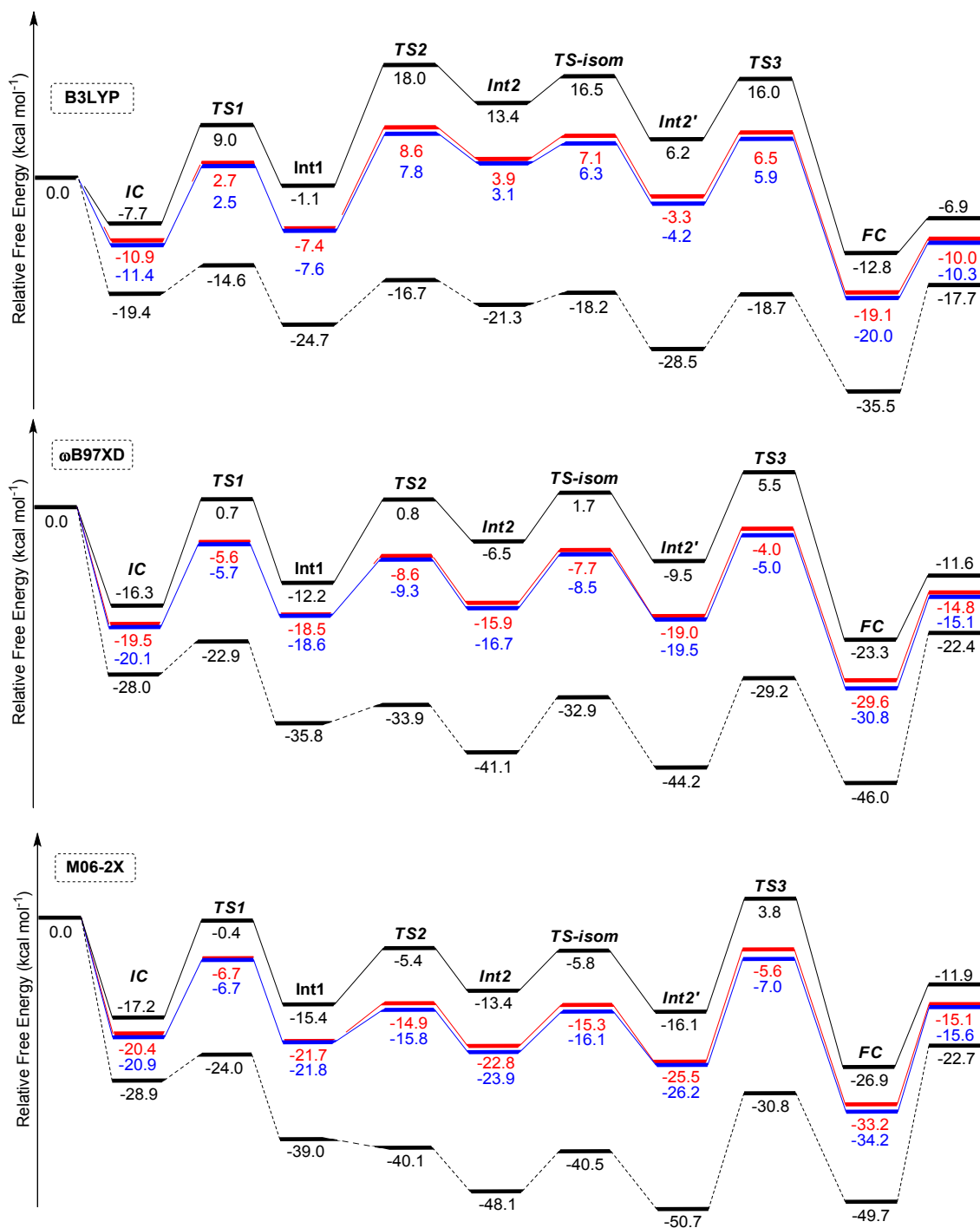
Figure S2. Free-energy profiles for cyclic carbonate formation from CO_2 and 1,2-epoxyhexane catalyzed by [Al{amino-tris(phenolate)}]/NBu_4I, calculated at different levels. The solid black line represents the pathway without considering any kind of corrections for entropy in solution, whereas the dashed black line stands for the pathway including only the vibrational and rotational terms in the calculation of the total entropy in solution. The pathways considering entropy corrections by Martin, and Wertz/Ziegler appear in red and blue, respectively.

4. Energetic Span Model

The energetic span model defined by Kozuch et al. take into account the entire Gibbs free energy profile, hence all the intermediates and transition states in the reaction pathway, contribute to the TOF. This approach is not equivalent to Eyring's equation, which only accounts the absolute Gibbs free energy barrier to calculate the TOF.

$$TOF = \frac{k_B \cdot T}{h} \cdot \frac{e^{-\Delta G_r/RT} - 1}{\sum_{i,j}^{N} e^{(T_i - I_j - \delta G'_{i,j})/RT}} = \frac{D_f}{K_r}$$

(eq. S1.4)

5. TOFs, Energetic Spans and TOF-determining species of the reaction. Geometry optimizations in gas-phase

Table S2. TOFs, energetic spans, and TOF-determining species for the Al-catalyzed formation of cyclic carbonate from CO_2 and 1,2-epoxyhexane. S_v+S_r stands for the entropic corrections by neglecting the translational contributions; M, for Martin corrections; and W/Z, for Wertz and Ziegler corrections.

Entropic corrections	δE (kcal·mol^{-1})	TOF (h^{-1})	TDI	TDTS
B3LYP_none	25.1	7.12	IC	TS2/TS-isom
B3LYP_S_v+S_r	19.6	1.8 x 10^4	FC	CC
B3LYP_M	19.4	1.6 x 10^4	Int1	TS2/TS-isom
B3LYP_W/Z	19.0	2.2 x 10^4	Int1	TS2/TS-isom
ωB97XD_none	23.7	1.17 x 10^2	IC	TS3
ωB97XD_S_v+S_r	25.9	2.33	FC	CC
ωB97XD_M	19.3	5.3 x 10^4	Int1/FC	TS3/CC
ωB97XD_W/Z	18.1	1.2 x 10^5	Int1	TS3
M06-2X_none	22.3	6.95 x 10^2	Int1	TS3
M06-2X_S_v+S_r	30.8	3.2 x 10^{-3}	Int2'	CC
M06-2X_M	19.2	5.3 x 10^4	Int1	TS3
M06-2X_W/Z	18.0	1.2 x 10^5	FC	CC

Exp. TOF = 9.6 x 10^2 h^{-1} (lowest value measured in the optimization studies of the activity of Al-catalyst) and 2.6 x 10^4 h^{-1} (highest value obtained in the stability studies using the Al-catalyst) depending on reactants and catalyst system concentrations.

6. Energetic Spans and TOFs for *Opt Gas* and *Opt Solv* free-energy profiles

Table S3. Energetic span and TOF values for the Al-catalyzed formation of cyclic carbonate from CO_2 and 1,2-epoxyhexane calculated at different DFT levels and including entropic corrections in solution.

Entropic corrections	Opt Gas	Opt Solvent	Opt Gas	Opt Solvent
	δE (kcal·mol^{-1})		TOF (h^{-1})	
B3LYP_none	25.1	25.7	7.12	7.24
B3LYP_S_v+S_r	19.6	17.9	1.8×10^4	2.6×10^5
B3LYP_M	19.4	19.4	1.6×10^4	3.9×10^4
B3LYP_W/Z	19.0	19.1	2.2×10^4	5.8×10^4
wB97XD_none	23.7	21.8	1.17×10^2	2.0×10^3
wB97XD_S_v+S_r	26.0	23.6	2.33	79.0
wB97XD_M	19.3	15.5	5.3×10^4	4.9×10^6
wB97XD_W/Z	18.1	15.8	1.2×10^5	3.4×10^6
M06-2X_none	22.4	21.1	6.95×10^2	4.6×10^3
M06-2X_S_v+S_r	30.9	28.0	3.2×10^{-3}	0.15
M06-2X_M	19.2	19.9	5.3×10^4	2.4×10^4
M06-2X_W/Z	18.0	19.2	1.2×10^5	4.0×10^4
Experimental	**19.7**		**3.6 x 10^4**	

Sv+Sr stands for the entropic corrections by neglecting the translational contributions; M, for Martin corrections; and W/Z, for Wertz and Ziegler corrections.

7. Entropy differences between uncorrected and Martin corrected profiles

In this section, we consider five structures of the energy profile. First, IC contains the epoxide and the catalyst, Int1 has three bodies bonded between each other (catalyst, epoxide and iodide) and Int2', TS2 and TS3 have the four bodies involved in the reaction, the catalyst, the 1,2-epoxyhexane, the iodide and the carbon dioxide. Consequently, as it can be seen below in Table S4, the entropy difference between TS2 and TS3 (four bodies) respect IC (two bodies) is 21.116 cal·mol^{-1} K^{-1}. On the other hand, when Int1 is considered, the entropy difference is 10.559 cal·mol^{-1} K^{-1}. Finally, TS2 and TS3 have the same mass (same number of bodies) than Int2', so no entropy variation is observed.

Table S4. Entropy difference between TDTS (TS2 or TS3) and TDI (IC, Int1 or Int2'). Particular entropy (cal·mol^{-1} K^{-1}) contributions and total entropy are showed for each DFT functional.

Entropy (S) [cal·mol^{-1} K^{-1}]	TS2-IC			TS2-IC			
	B3LYP	wB97XD	M06-2X	B3LYP_M	wB97XD_M	M06-2X_M	M-none
Total	-69,759	-65,914	-71,028	-48,643	-44,797	-49,912	**21,116**
Elec	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Trans	-77,014	-77,014	-77,014	-55,898	-55,898	-55,898	**21,116**
Rot	-12,219	-12,162	-12,104	-12,219	-12,162	-12,104	0,000
Vib	19,475	23,263	18,091	19,475	23,263	18,091	0,000

Entropy (S) [cal·mol^{-1} K^{-1}]	TS3-IC			TS3-IC			
	B3LYP	wB97XD	M06-2X	B3LYP_M	wB97XD_M	M06-2X_M	M-none
Total	-67,138	-72,539	-78,793	-46,021	-51,423	-57,677	**21,116**
Elec	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Trans	-77,014	-77,014	-77,014	-55,898	-55,898	-55,898	**21,116**
Rot	-11,757	-11,945	-12,127	-11,757	-11,945	-12,127	0,000
Vib	21,634	16,421	10,348	21,634	16,421	10,348	0,000

Entropy (S) [cal·mol^{-1} K^{-1}]	TS3-Int1			TS3-Int1			
	B3LYP	wB97XD	M06-2X	B3LYP_M	wB97XD_M	M06-2X_M	M-none
Total	-39,266	-49,295	-54,001	-28,707	-38,736	-43,442	**10,559**
Elec	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Trans	-37,108	-37,108	-37,108	-26,550	-26,550	-26,550	**10,559**
Rot	-12,553	-12,749	-12,932	-12,553	-12,749	-12,932	0,000
Vib	10,396	0,564	-3,960	10,396	0,564	-3,960	0,000

Entropy (S) [cal·mol^{-1} K^{-1}]	TS3-Int2'			TS3-Int2'			
	B3LYP	wB97XD	M06-2X	B3LYP_M	wB97XD_M	M06-2X_M	M-none
Total	4,730	-9,483	-12,351	4,730	-9,484	-12,350	0,000
Elec	0,000	0,000	0,000	0,000	0,000	0,000	**0,000**
Trans	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Rot	0,111	-0,044	-0,143	0,111	-0,044	-0,143	**0,000**
Vib	4,619	-9,439	-12,207	4,619	-9,439	-12,207	0,000

8. References

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