Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: The effect of the environment on the reaction mechanism of the methyl transfer reaction between trimethylsulfonium and phenolate.

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1 Effect of SMD continuous solvent on the energy profile of the transmethylation reaction.

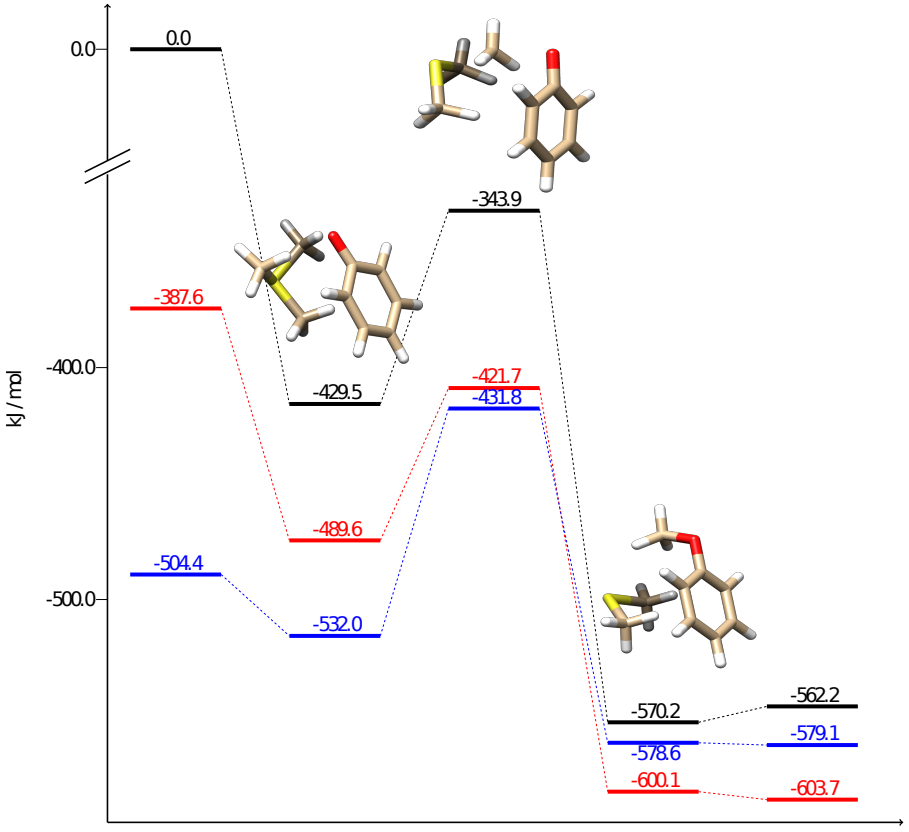

Figure 1: Potential energy change for the reaction occurring in vacuum (black), diethyl ether-SMD (red) and water (blue) environments. It spans from isolated reactants to isolated products.

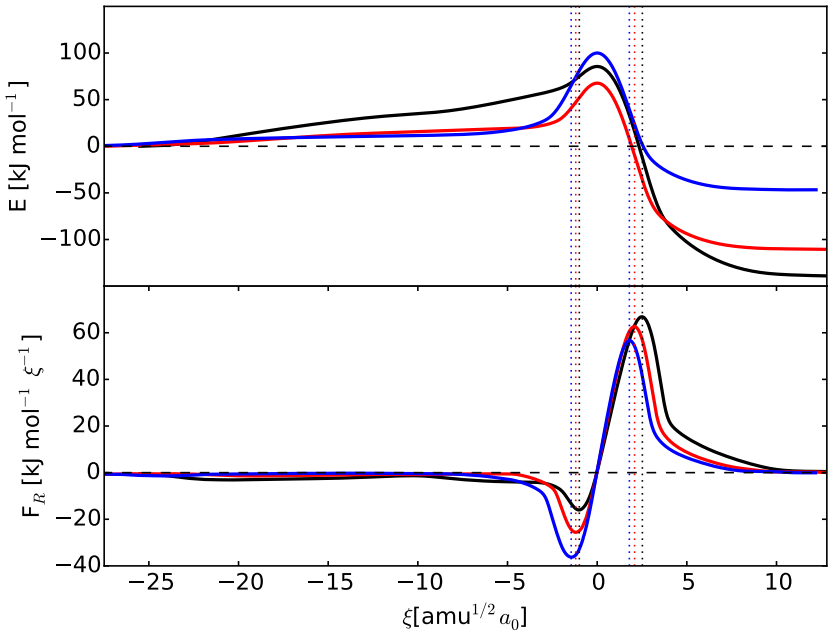

Figure 2: Potential energy (top) and reaction force (bottom) profiles for methyl transfer ocurring in vacuum (black), diethyl ether-SMD (red) and water-SMD (blue) environments. Vertical dotted lines show the points where reaction force is minimized and maximized for each case.

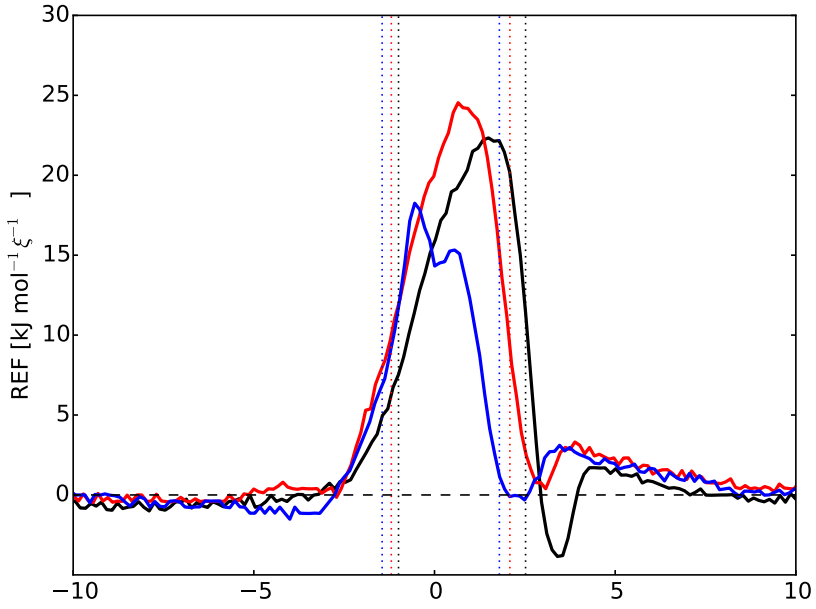

Figure 3: Reaction electronic flux for methyl transfer ocurring in vacuum (black), diethyl ether-SMD (red) and water-SMD (blue) environments. Vertical dotted lines show the points where reaction force is minimized and maximized for each case.

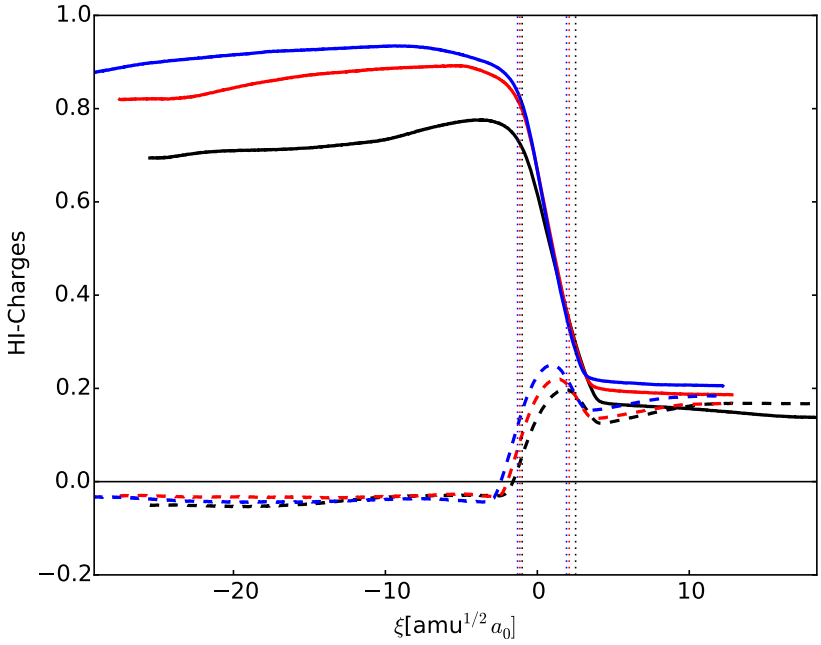

Figure 4: Evolution of Hirshfeld-I charges along IRC in vacuum (black), diethyl ether-SMD (red) and water-SMD (blue) environments. Continuous lines represent the charge on TMS molecule. Dashed lines show charges on atoms belonging to the transferred methyl group. Vertical dotted lines show the points where the reaction force is minimized and maximized for each case.

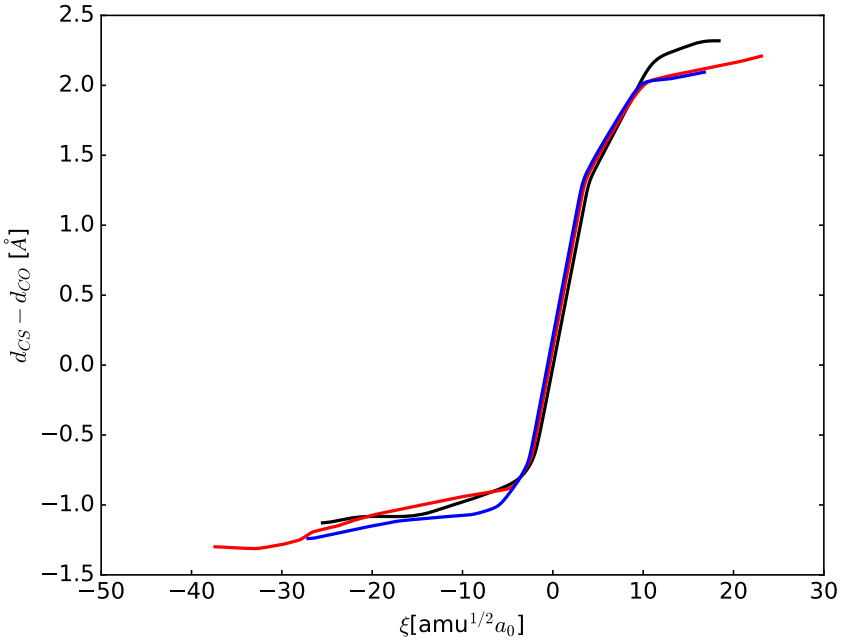

Figure 5: Evolution of the difference of distance between broken (C-S) and formed (C-O) bonds against ξ in vacuum (black), diethyl ether-PCM (red) and water-PCM (blue) environments.

Table S1. Results obtained through G09 calculations on different chemical species involved in the reaction. Level of theory:M06-2X/6-311G+(d,p). Temperature: 298.15 K.

HF Energy

	TMS	Phenolate	TS	DMS	Anisole
	[E_h]	[E_h]	[E_h]	[E_h]	[E_h]
vacuum	-517.6177276	-306.8572403	-824.6059478	-477.9777979	-346.7113042
DEE/SMD	-517.6931917	-306.929415	-824.635595	-477.9833182	-346.7215746
WAT/SMD	-517.7080849	-306.9590203	-824.6394131	-477.979209	-346.7163259
DEE/PCM	-517.6830511	-306.9275492	-824.6251154	-477.9804024	-346.71492
WAT/PCM	-517.7023595	-306.9507626	-824.6338257	-477.9816975	-346.7168571

	TMS	Phenolate	TS	Barrier	React. ener
	[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]
vacuum	-1359005.344	-805653.6844	-2165002.916	-343.8877275	-562.2093421
DEE/SMD	-1359203.475	-805843.1791	-2165080.755	-34.10071601	-216.0421555
WAT/SMD	-1359242.577	-805920.9078	-2165090.779	72.70560855	-74.64217735
DEE/PCM	-1359176.851	-805838.2804	-2165053.24	-38.10948957	-222.4379654
WAT/PCM	-1359227.545	-805899.2272	-2165076.109	50.66253993	-119.2829369

Free Energies

	TMS	Phenolate	TS	DMS	Anisole
	[E_h]	[E_h]	[E_h]	[E_h]	[E_h]
vacuum	-517.531432	-306.794911	-824.437584	-477.928675	-346.608188
DEE/SMD	-517.606698	-306.866744	-824.467756	-477.934598	-346.619231
WAT/SMD	-517.621357	-306.896119	-824.473262	-477.93046	-346.614546
DEE/PCM	-517.596412	-306.864769	-824.456652	-477.93132	-346.611962
WAT/PCM	-517.615616	-306.887872	-824.466871	-477.93261	-346.613926

	TMS	Phenolate	TS	Barrier	React. ener
	[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]
vacuum	-1358778.775	-805490.0388	-2164560.877	-292.0632455	-552.72026
DEE/SMD	-1358976.386	-805678.6364	-2164640.093	14.928593	-211.0560685
WAT/SMD	-1359014.873	-805755.7604	-2164654.549	116.083857	-72.280015
DEE/PCM	-1358949.38	-805673.451	-2164610.94	11.8908895	-215.5561755
WAT/PCM	-1358999.8	-805734.1079	-2164637.77	96.1379335	-113.022524

Enthalpies

	TMS	Phenolate	TS	DMS	Anisole
	[E_h]	[E_h]	[E_h]	[E_h]	[E_h]
vacuum	-517.494523	-306.759878	-824.383665	-477.895848	-346.569615
DEE/SMD	-517.56992	-306.831749	-824.413213	-477.901514	-346.580181
WAT/SMD	-517.584784	-306.861215	-824.41738	-477.897424	-346.575057
DEE/PCM	-517.559459	-306.829803	-824.403818	-477.898481	-346.573344
WAT/PCM	-517.578811	-306.85297	-824.411372	-477.899784	-346.575321

TMS	Phenolate	TS	Barrier	React. ener
[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]
-1358681.87	-805398.0597	-2164419.312	-339.382632	-554.143281
-1358879.825	-805586.757	-2164496.891	-30.308772	-210.108263
-1358918.85	-805664.12	-2164507.831	75.1391845	-69.528491
-1358852.36	-805581.6478	-2164472.224	-38.216778	-216.7691565
-1358903.168	-805642.4727	-2164492.057	53.5838295	-113.747162

Table S2. Points of the coordinate along IRC performed in G09, where the minimum and maximum values for Reaction Force can be found. Level of theory: M06-2X/6-311G+(d,p).

	Coordinate	
	Reaction Force Minimum	Reaction Force Maximum
vacuum	-0.996	2.52
DEE-PCM	-1.15	2.1
WAT-PCM	-1.3	1.92
DEE-SMD	-1.19572	2.08552
WAT-SMD	-1.4495	1.79532