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Supporting Information

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The Rates of S_N2 Reactions and their Relation to Molecular and Solvent Properties

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TABLE S1. Data employed in the making of Figure 1.

<i>Systems</i>	$l_{\text{CX}}^{\ddagger}(\text{ISM})$	$l_{\text{CX}}^{\ddagger}(\text{ab initio})$	<i>References</i>
$\{\text{H}\cdots\text{H}\cdots\text{H}\}^{-}$	0.92840	1.0580	[1]
$\{\text{F}\cdots\text{CH}_3\cdots\text{F}\}^{-}$	1.7305	1.7810	[2]
$\{\text{Cl}\cdots\text{CH}_3\cdots\text{Cl}\}^{-}$	2.2355	2.3070	[2]
$\{\text{Br}\cdots\text{CH}_3\cdots\text{Br}\}^{-}$	2.4205	2.4440	[2]
$\{\text{I}\cdots\text{CH}_3\cdots\text{I}\}^{-}$	2.6700	2.6730	[3]

TABLE S2. Data employed in the making of Figure 2.

<i>Systems</i>	$\Delta V_{\text{Cl}}^{\ddagger}(\text{ISM})$	$\Delta V_{\text{ad}}^{\ddagger}(\text{ab initio})$	<i>References</i>
$\text{CH}_3\text{CH}_2^{-} + \text{CH}_3\text{CH}_2\text{CH}_3$	49.600	44.700	[4]
$\text{CH}_3\text{NH}^{-} + \text{CH}_3\text{NHCH}_3$	33.100	29.300	[4]
$\text{CH}_3\text{O}^{-} + \text{CH}_3\text{OCH}_3$	25.900	19.500	[4]
$\text{F}^{-} + \text{CH}_3\text{F}$	19.190	13.300	[5]
$\text{CH}_3\text{S}^{-} + \text{CH}_3\text{SCH}_3$	19.300	21.900	[4]
$\text{Cl}^{-} + \text{CH}_3\text{Cl}$	13.430	13.610	[5]
$\text{Br}^{-} + \text{CH}_3\text{Br}$	12.550	10.800	[5]
$\text{I}^{-} + \text{CH}_3\text{I}$	11.740	9.6000	[5]
$\text{F}^{-} + \text{CH}_3\text{Cl}$	5.8800	2.8900	[5]
$\text{F}^{-} + \text{CH}_3\text{Br}$	4.9500	0.64000	[5]
$\text{F}^{-} + \text{CH}_3\text{I}$	4.1100	0.20000	[6]
$\text{Cl}^{-} + \text{CH}_3\text{Br}$	10.320	8.6100	[5]
$\text{Cl}^{-} + \text{CH}_3\text{I}$	7.5100	7.6000	[6]
$\text{Br}^{-} + \text{CH}_3\text{I}$	8.9100	9.2000	[6]

TABLE S3. Data employed in the making of Figure 4.

<i>Medium</i>	<i>Acceptor Number</i> [7]	$\Delta V_{\text{ad}}^{\ddagger}(\text{gas phase})$ or $E_{\text{a}}(\text{solution})$	<i>References</i>
Gas phase	0	9.6000	[5]
Acetone	12.5	13.5	[8]
Ethanol	37.1	15.6	[8]
Methanol	41.5	16.0	[8]

Ethylene glycol	43.5	16.8	[8]
Water	54.8	18.1	[8]

TABLE S4. Data employed in the making of Figure 6.

<i>Reactants</i>	<i>Solvent</i>	ΔV^0 (kcal mol ⁻¹)	$k_{\text{ISM}} / 10^{-4}$ (M ⁻¹ s ⁻¹)	$k_{\text{exp}} / 10^{-4}$ (M ⁻¹ s ⁻¹)	<i>References</i>
F ⁻ + CH ₃ Cl	Water	-1.1 ^[9]	0.00012	0.00014	^[10]
F ⁻ + CH ₃ Br	Water	-2.7 ^[9]	0.0013	0.00302	^[10]
F ⁻ + CH ₃ I	Water	-0.7 ^[10]	0.00069	0.000692	^[10]
Cl ⁻ + CH ₃ Br	Water	-1.3 ^[9]	0.49	0.079	^[11]
Cl ⁻ + CH ₃ I	Water	1.1 ^[10]	0.19	0.032	^[10]
Br ⁻ + CH ₃ I	Water	1.2 ^[10]	0.55	0.40	^[11]
I ⁻ + CH ₃ I	Water	0	4.4	4.85	^[10]
OH ⁻ + CH ₃ F	Water	-22.5 ^[12]	0.00013	0.00586	^[10]
OH ⁻ + CH ₃ Cl	Water	-22.0 ^[12]	0.37	0.0667	^[10]
OH ⁻ + CH ₃ Br	Water	-23.4 ^[12]	2.1	1.435	^[10]
OH ⁻ + CH ₃ I	Water	-21.3 ^[12]	1.5	0.636	^[10]
Cl ⁻ + CH ₃ I	Acetone	-4.9 ^[10]	240,000	49,000	^[11]
Br ⁻ + CH ₃ I	Acetone	-1.9 ^[11]	65,000	100,000	^[11]
I ⁻ + CH ₃ I	Acetone	0	30,000	63,000	^[8]

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