Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Mechanism and Regioselectivity in Methylation of Nitronates $[CH_2NO_2]^-$: Resonance vs Inductive Effects

Ayyaz Mahmood,[†,‡] Tehmina Akram,[+] Maryam Kiani,[‡] Tayyaba Akram,[≠] Xiaoqing Tian,[‡*] and Yiwen Sun[†*]

[†]National-Regional Key Technology Engineering Laboratory for Medical Ultrasound, Guangdong Key Laboratory for Biomedical Measurements and Ultrasound Imaging, Department of Biomedical Engineering, School of Medicine, Shenzhen University, Shenzhen 518060, China.
[‡]College of Physics and Optical Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China.
[+]CAS Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Department of Chemistry, University of Science and Technology of China, Hefei 230026, China.
[≠]Department of Physics, COMSATS Institute of Information Technology, Lahore 54000, Pakistan.

*Corresponding authors: ywsun@szu.edu.cn and xqtian@szu.edu.cn

Electronic Supplementary Information

Contents

1.1 Trends in Vinylogue Extrapolation Results

Figure S1. Plots of $\Delta E_{res}(n)$ versus the Hückel charges on nucleophilic atoms for reactions in solutions.

Figure S2. Plots of $\Delta E_{ind}(n)$ versus the n for reactions in solutions.

Table S1. Comparison of energy values calculated using SMD and PCM solvation models.

Table S2. Calculated imaginary frequencies (cm^{-1}) for transition states.

Table S3. Vinylogue Extrapolation results for the C/O-methylation

1.1 Trends in Vinylogue Extrapolation Results

There are several observations that can be seen in Table S1 and Table S2 and plots in Figure 4 and Figure S4 including which are i) the acidic character of vinylogues increases with the increasing value of *n*. This is due to the increasing stabilization of conjugate base as a result of increasing resonance with increasing value of *n*. ii) each parallel vinylogue is stronger acid than the corresponding perpendicular vinylogue. This is due to the reason that the negatively charged electron-withdrawing group is perpendicular to the vinyl groups which decreases or completely turns off the resonance contribution from the terminal group. iii) Each perpendicular vinylogue is stronger acid than the corresponding reference vinylogue which indicate the role of inductive effect. iv) the both resonance and inductive effect contribution decreases with the increasing value of *n* due the increasing chain length.

Table S1. Comparison of energy values calculated using SMD and PCM solvation models.

		$E_{perp}^{\ddagger}$	$E_{plan}^{\ddagger}$	$E_{ref}^{\ddagger}$	ΔE_{res}	ΔE_{ind}
PCM	*C-methylation*	53.04	56.14	39.86	−3.11	−13.17
	O-methylation	34.37	67.62	9.90	−33.25	−24.47
DCM	*C-methylation*	54.03	56.98	40.19	−2.95	−13.84
	O-methylation	34.687	68.3262	10.03	−33.6392	−24.657

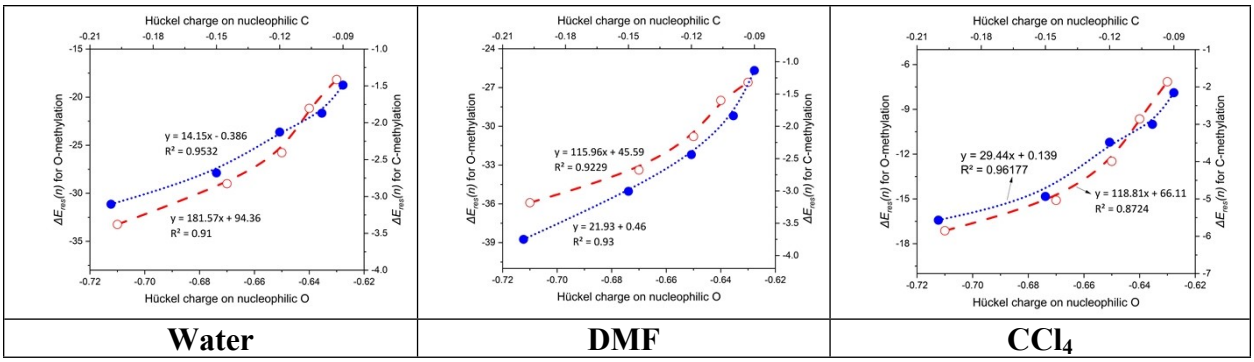

Fig. S1. Plots of $\Delta E_{res}(n)$ versus the Hückel charges on nucleophilic atoms for reactions in the gas-phase. The resonance contribution towards the reaction energy barrier for each vinylogues is plotted against the calculated Hückel charge on nucleophilic carbon (C-methylation), shown in filled circles (●), and on nucleophilic oxygen (O-methylation) shown in unfilled circles (○). The corresponding x- and y-axis for C-methylation are on the top and on the right. Energy units in kJ mol^{-1}.

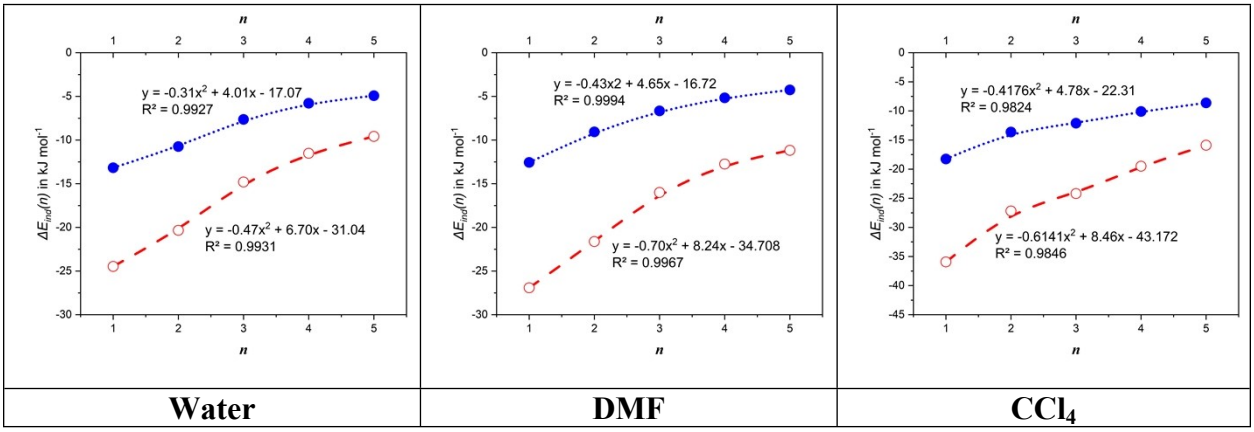

Fig. S2. Plots of $\Delta E_{ind}(n)$ versus the *n* for reactions in solution phase. The inductive effect contribution towards the reaction energy barrier for each vinylogues is plotted for C-methylation shown in blue line with filled circles (●), and for O-methylation shown in red line with unfilled circles (○).

Table S2. Calculated imaginary frequencies (cm^{-1}) for transition states of the C-methylation and O-methylation pathways for parent nitronate (n = 0) in the gas-phase, $[CH_2NO_2]^-$ + CH_3I**,** computed at different theoretical levels.

TS	MP2/ LAN	MP2/ DZ	B2PLYP/ LAN	B2PLYP / DZ	mPW2PLYP / LAN	mPW2PLYP/ DZ
TS@C	−473.5	−445.5	−335.6	−302.7	−358.8	−331.5
TS@O	−515.1	−519.7	−394.8	−381.3	−404.8	−391.6

Table S3. Vinylogue Extrapolation results for the C/O-methylation in kJ/mol. Calculations at M062X/6-311++g(d,p)/LANL2DZdp in solution phase for the reaction with substrate CH_3I.

	C-methylation					
	n	$E_{perp}^{\ddagger}$	$E_{plan}^{\ddagger}$	$E_{ref}^{\ddagger}$	ΔE_{res}	ΔE_{ind}
Water	0	N/A	45.48	24.83	(−4.21)	(−17.08)
	1	53.04	56.14	39.86	−3.11	−13.17
	2	60.77	63.45	50.02	−2.68	−10.75
	3	65.13	67.25	57.49	−2.13	−7.64
	4	73.22	75.09	67.43	−1.87	−5.79
	5	81.85	83.34	76.92	−1.49	−4.93
	O-methylation					
	0	N/A	56.44	−6.48	(−38.18)	(−31.05)
	1	34.37	67.62	9.90	−33.25	−24.47
	2	47.42	76.43	27.08	−29.01	−20.34
	3	57.98	83.75	43.17	−25.78	−14.80
	4	69.46	90.62	57.94	−21.16	−11.52
	5	77.03	95.20	67.44	−18.17	−9.58
DMF	*C-methylation*					
	0	N/A	44.40	23.85	(−5.47)	(−16.73)
	1	51.97	55.32	39.41	−3.35	−12.56
	2	59.69	62.85	50.62	−3.16	−9.07
	3	66.28	68.72	59.61	−2.44	−6.67
	4	73.82	75.66	68.65	−1.84	−5.17
	5	78.83	79.97	74.57	−1.14	−4.26
	O-methylation					

	0	N/A	55.48	−13.19	(−39.06)	(−34.71)
	1	32.95	68.87	6.03	−35.91	−26.92
	2	45.58	78.97	23.96	−33.39	−21.62
	3	56.48	87.27	40.47	−30.79	−16.01
	4	64.25	92.25	51.50	−28.00	−12.75
	5	71.36	97.96	60.18	−26.60	−11.18
CCl_4	*C-methylation*					
	0	N/A	23.74	−5.83	(−6.46)	(−22.31)
	1	27.70	33.27	9.43	−5.57	−18.27
	2	40.83	45.76	27.20	−4.93	−13.62
	3	52.72	52.20	40.61	−3.48	−12.11
	4	64.40	59.40	54.30	−3.00	−10.10
	5	75.52	66.68	66.90	−2.15	−8.62
	O-methylation					
	0	N/A	34.53	−17.71	(−20.61)	(−43.17)
	1	23.88	41.01	−12.06	−17.13	−35.94
	2	37.72	52.81	10.53	−15.09	−27.19
	3	48.46	64.93	24.27	−12.48	−24.19
	4	56.86	75.50	37.36	−9.64	−19.50
	5	64.26	86.41	48.37	−7.15	−15.89