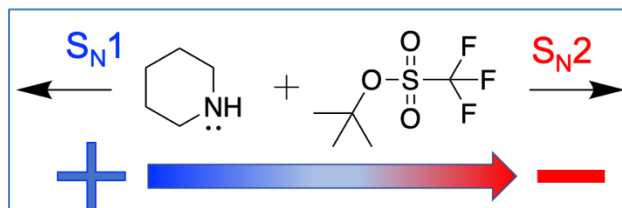


Electrostatic Switching Between S_N1 and S_N2 Pathways

Li-Juan Yu, Michelle L. Coote*

ARC Centre of Excellence for Electromaterials Science, Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, 2601, Australia

ABSTRACT: A test set 264 nucleophilic substitution reactions was studied via accurate quantum chemical reactions to establish the relative preferences for S_N1 versus S_N2 mechanisms. In low polar solvents, reactions involving anionic nucleophiles and leaving groups favored S_N2 pathways. In contrast, S_N1 is preferred for those reactions involving neutral nucleophiles and leaving groups except where the carbocation intermediates are exceptionally unstable. For neutral nucleophiles and anionic leaving groups S_N2 is generally preferred over S_N1 except for exceptionally stable carbocation intermediates. On the basis of these studies, candidate reactions for which distinct S_N1 or S_N2 preferences could be reversed by electric fields were selected. As proof of concept, the S_N1 / S_N2 preferences for the reaction of tBu-triflate with pyridine (S_N2 to S_N1) and with piperidine (S_N1 to S_N2) were switched by both charged functional groups and point charges (i.e. electric fields) along the reaction axis, with a positive charge on the nucleophile side favoring S_N1 and a negative charge favoring S_N2 for these reactions.



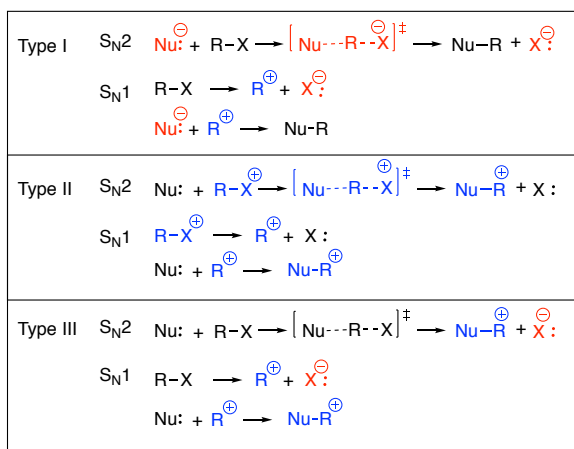
INTRODUCTION

The use of electric fields to manipulate chemical reactions, while well understood theoretically,^{1,2} is only now entering mainstream chemistry as a tool to manipulate chemical processes.³ The basic underlying principle is that most neutral species have some degree of polarity and hence can be electrostatically stabilized by an appropriately aligned electric field. If these effects change over the course of reaction, as they often do, then net changes to reaction barriers and energies are possible. The challenge is to deliver a significant enough electric field and to control the orientation of reagents in that field. Experiments have shown that this can be achieved at the nanoscale using scanning tunneling microscopy,^{4,5} and, at larger scales, using electrodes⁶ charged insulators,⁷ charged functional groups,⁸⁻¹⁰ and metal ions.¹¹⁻¹³

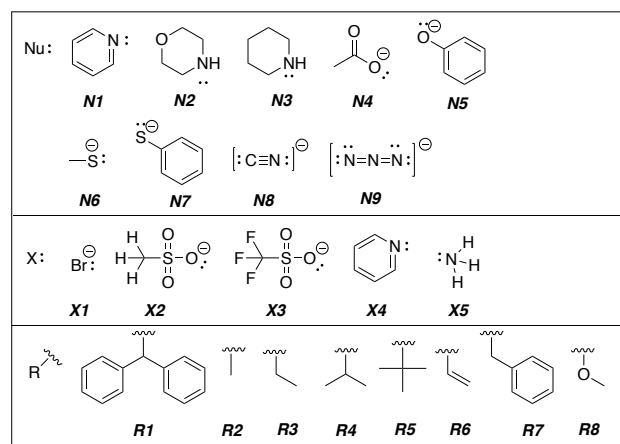
While catalysis has been the main focus until now,¹⁻¹⁵ perhaps the most interesting applications stem from the ability of electric fields to change outcome of a reaction. For instance, theoretical studies have shown that the regio- and stereoselectivity of a Diels-Alder reaction can be changed with either external oriented fields^{16,17} or appropriately placed charged functional groups.¹⁸ Theoretical studies have also shown that charged functional groups can be used to selectively stabilize or destabilize the relative energies of different excited states in acetophenone derivatives.¹⁹ This ability to switch the outcome of a reaction results from the differing polarities and polarizabilities of alternative energy levels or transition states. The present work uses theory to explore whether and under what conditions an electrostatic switch between an S_N2 nucleophilic substitution and an S_N1 mechanism might be possible.

Nucleophilic substitution is an important fundamental textbook reaction in organic synthesis. As is well known, it can proceed via a concerted bimolecular (S_N2) pathway that involves inversion of the stereochemistry, or a two-step (S_N1) pathway that leads to a racemic mixture of products. The reactivity trends have been extensively studied²⁰ and are dominated by the relative stabilities of the nucleophile (Nu) and leaving group (X), as well as the substrate-derived carbocation (R⁺). The polarizability of the nucleophile also plays a role (the “hard” / “soft” nucleophile concept). The rate determining steps in each pathway involve different charged intermediates and so it is an obvious candidate for electrostatic switching. Indeed, recent work by Shaik and co-workers has shown that external electric fields aligned along the reaction axis can lower or raise the barrier heights for the S_N2 reaction of pyridine and its derivatives with methyl iodide,²¹ a reaction better known as the Menshutkin reaction.²² This builds on their earlier work analyzing the effects of local electric fields from metal cations on bond activation.²³

These reactions are examples of a “Type III” process in Scheme 1 and as such it makes sense that field aligned along the reaction axis will stabilize or destabilize the charge separated transition state and products more than the reactants, depending on its orientation. In that work, in which the reaction was simulated with gold thiolate linkers to mimic STM experiments, the authors also noted a mechanistic cross-over involving electron transfer to gold at high field strengths.²¹ However, a comparison of S_N2 versus S_N1 cross-over, the aim of the present work, was not undertaken. Nonetheless other studies have shown for certain reagents S_N1 and S_N2 occur in competition with each other.²⁴

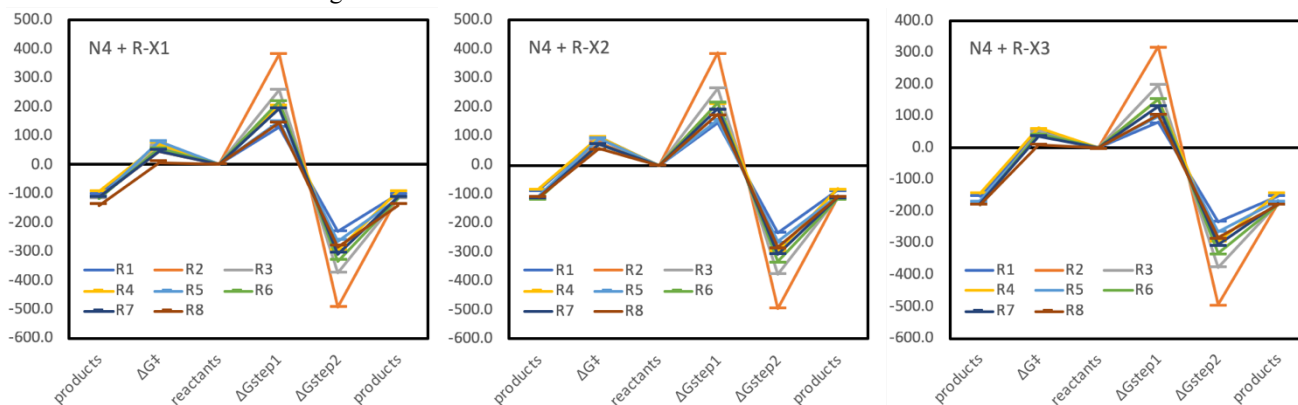


Scheme 1. The three scenarios considered according to the charge on the nucleophile and leaving group: Type I conserves charge in the S_N2 process but not step 1 of the competing S_N1 process; Type II conserves charge in both the S_N2 process and both steps of the S_N1 process; Type III conserves charge in neither the S_N2 or step 1 of the competing S_N1 process.



Scheme 2. Test set in the present work.

In the present work we use computational chemistry to identify target reactions for which the S_N2 versus S_N1 preferences are close enough that electric fields of experimentally accessible magnitudes (either in an STM experiment or from charged functional groups) and can reverse those preferences. In doing this, we will consider three different scenarios according to whether or not charge is conserved in the various steps (Scheme 1). Given that charge separation is energetically unfavorable, even in solution, it was thought that the different scenarios would have significant differences in their



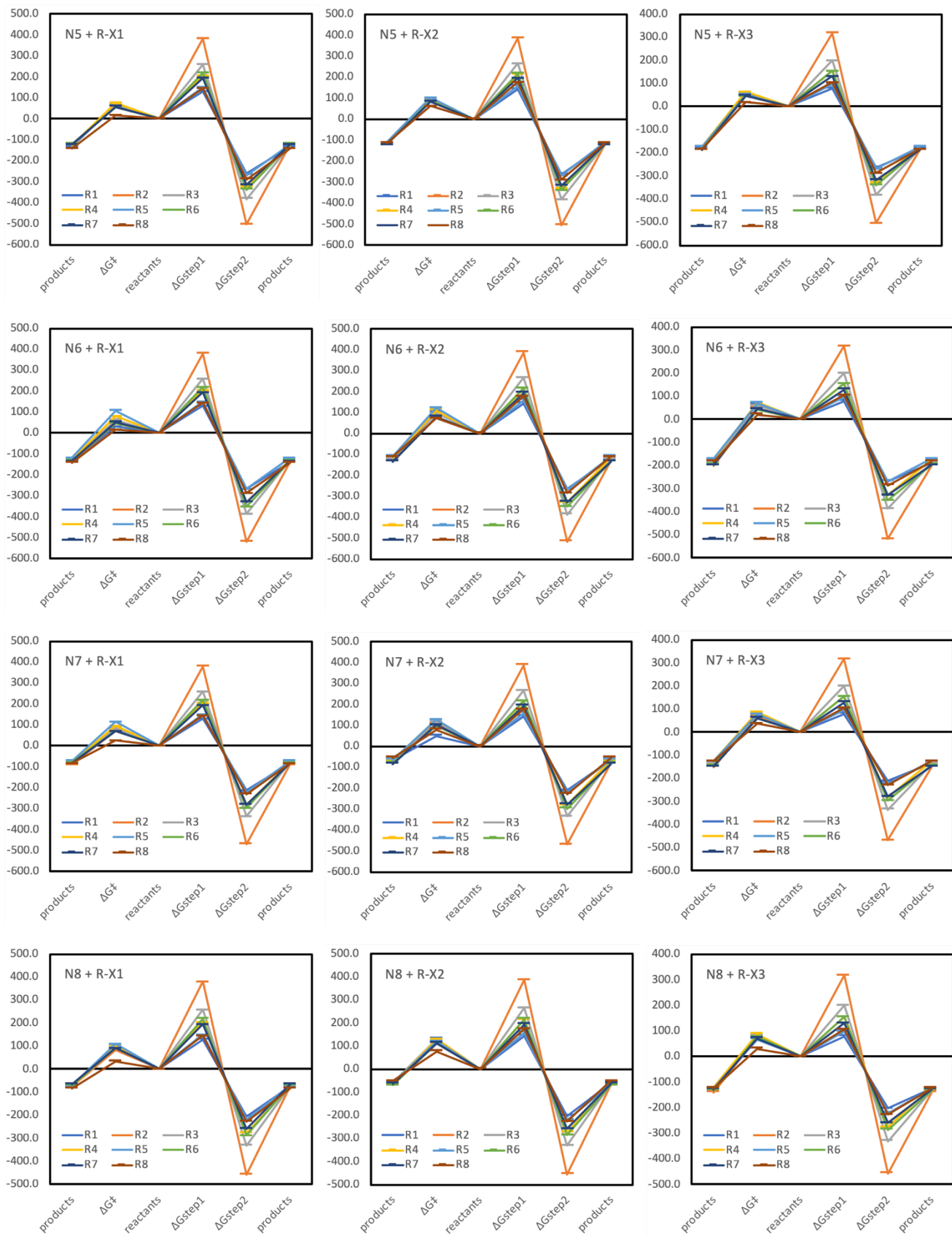
relative S_N1 versus S_N2 preferences. The differences between these scenarios stem from the charges on the nucleophile Nu and/or the leaving group X. The species examined in the present work are shown in Scheme 2. In what follows we study the S_N2 versus S_N1 reactivity preferences in the absence of field and, for those reaction in which the differences are smallest, we then show the effect of field on these preferences.

COMPUTATIONAL PROCEDURES

The principle aim was to study the effect of external electric field on the reaction barrier heights, rather than assess absolute energies. For this purpose, the M06-2X/6-31+G(d) level of theory was sufficient to use in this study. This level of theory has been previously shown to provide an accurate measure of the effect of electric fields upon a range of chemical processes.^{4,8} All geometry optimizations and frequency calculations were carried out at this level of theory. Entropies, thermal corrections and zero-point vibrational energies were scaled by recommend scale factors.²⁵ All geometries were verified either as local minima (possessing no imaginary frequencies) or transition states (possessing only one imaginary frequency). Solvent Gibbs free energies in dichloromethane, acetone and DMSO were obtained via the direct method,²⁶ using the SMD²⁷ solvent model at the same level of theory. All the calculations were performed using Gaussian 09 software package, revision E.01.²⁸

RESULTS AND DISCUSSION

Type I reactions. The Type I reactions in Scheme 2 involve the negatively charged nucleophiles (N4-N9) and leaving groups (X1-X3) and charge is conserved in the S_N2 step but charge separation occurs in the rate determining first step of the S_N1 process. As such, one would expect a general preference for S_N2 , which would increase as the solvent becomes less polar and/or the charged intermediates become less stable. Taking dichloromethane as a typical low polar solvent for which charged species are still usually soluble, the potential energy surface for the competing S_N1 and S_N2 processes is shown in Figure 1. The numbers used to produce these graphs (see Tables S1–S6) and corresponding diagrams for other solvents (see Figures S1–S12) are shown in the Supporting Information. It should be noted that for the S_N2 reactions the barrier height is plotted; for S_N1 only the reaction energies. This is because the two S_N1 steps tend not to have saddle points and so the reaction energy provides a reasonable first estimate of the reaction barrier. The energy differences between this S_N1 step 1 ΔG and the S_N2 ΔG^\ddagger are summarized in Figure 2.



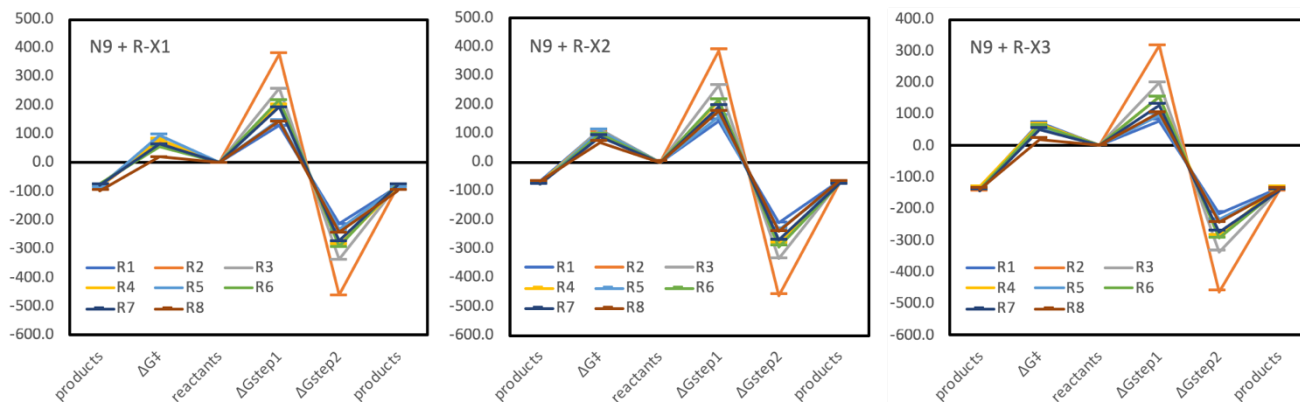


Figure 1. Gibbs free energy surfaces (kJ mol^{-1} 298.15K, dichloromethane) showing competing $\text{S}_{\text{N}}2$ (LHS of each plot) and $\text{S}_{\text{N}}1$ (RHS) processes as a function of R-group for the Type I reactions involving combinations of anionic nucleophiles N4 and N5 and anionic leaving groups X1–X3. For structures of all species see Scheme 2.

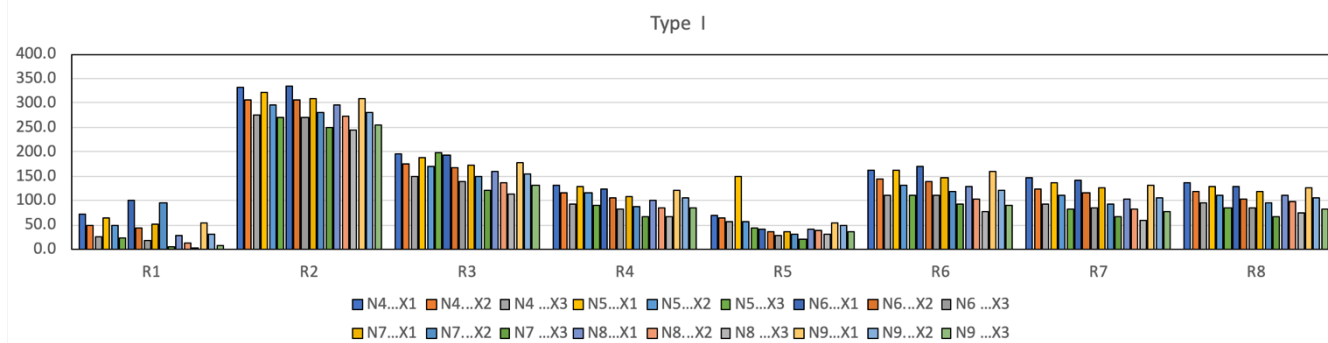


Figure 2. Gibbs free energy differences (kJ mol^{-1} 298.15K, dichloromethane) between the energy bottle necks for $\text{S}_{\text{N}}1$ (step 1 ΔG) and $\text{S}_{\text{N}}2$ (ΔG^\ddagger) as a function of R-group for the Type I reactions involving combinations of anionic nucleophiles N4–N9 and anionic leaving groups X1–X3. Differences are defined such that a positive number indicates that $\text{S}_{\text{N}}2$ is preferred. For structures of all species see Scheme 2.

As expected, the $\text{S}_{\text{N}}2$ process is preferred over $\text{S}_{\text{N}}1$ for this group of reactions. However, unsurprisingly, $\text{S}_{\text{N}}1$ becomes relatively more favorable as R^+ and X^- become more stable with the smallest differences between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ for highly stabilized $^+\text{CH}(\text{Ph})_2$ (R1) and $^+\text{C}(\text{CH}_3)_3$ (R5) carbocations, particularly with the stable triflate (X3) leaving group. At the other extreme, for the unstable CH_3^+ the preference for $\text{S}_{\text{N}}2$ is 240–335 kJ mol^{-1} for the 18 combinations of leaving groups and nucleophiles studied. In more polar solvents, the $\text{S}_{\text{N}}1$ versus $\text{S}_{\text{N}}2$ differences are smaller, due to the greater stability of the ionic intermediates in the $\text{S}_{\text{N}}1$ process (see Figures S1–S12 in Supporting Information). While it would be tempting to thus work in more polar solvents, it needs to be remembered that electrostatic effects tend to be screened by the solvent more effectively under these conditions.

Type II reactions. The “Type II” reactions involve the neutral nucleophiles (N1–N3) and leaving groups (X4–X5). Charge is conserved in both the $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$ steps and as such both processes are expected to be competitive with one another. This is clear from Gibbs free energy differences between the energy bottlenecks in each pathway (Figure 3) and the Gibbs free energy surfaces (Figure 4). Now the differences are generally smaller, and $\text{S}_{\text{N}}1$ is actually favored for the stable carbocations (e.g. R1 and R5). In practical terms, the Type II

reactions for which $\text{S}_{\text{N}}1$ / $\text{S}_{\text{N}}2$ switching is most likely under an electric field are those involving R1 and R5 ($\text{S}_{\text{N}}1$ to $\text{S}_{\text{N}}2$) and R4 ($\text{S}_{\text{N}}2$ to $\text{S}_{\text{N}}1$).

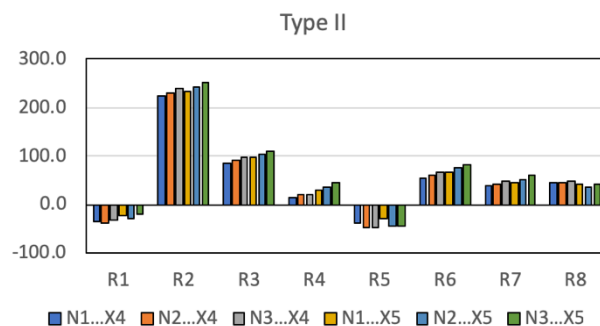


Figure 3. Gibbs free energy differences (kJ mol^{-1} 298.15K, dichloromethane) between the energy bottle necks for $\text{S}_{\text{N}}1$ (step 1 ΔG) and $\text{S}_{\text{N}}2$ (ΔG^\ddagger) as a function of R-group for the Type II reactions involving combinations of neutral nucleophiles (N1–N3) and neutral leaving groups X4–X5. Differences are defined such that a positive number indicates that $\text{S}_{\text{N}}2$ is preferred. For structures of all species see Scheme 2.

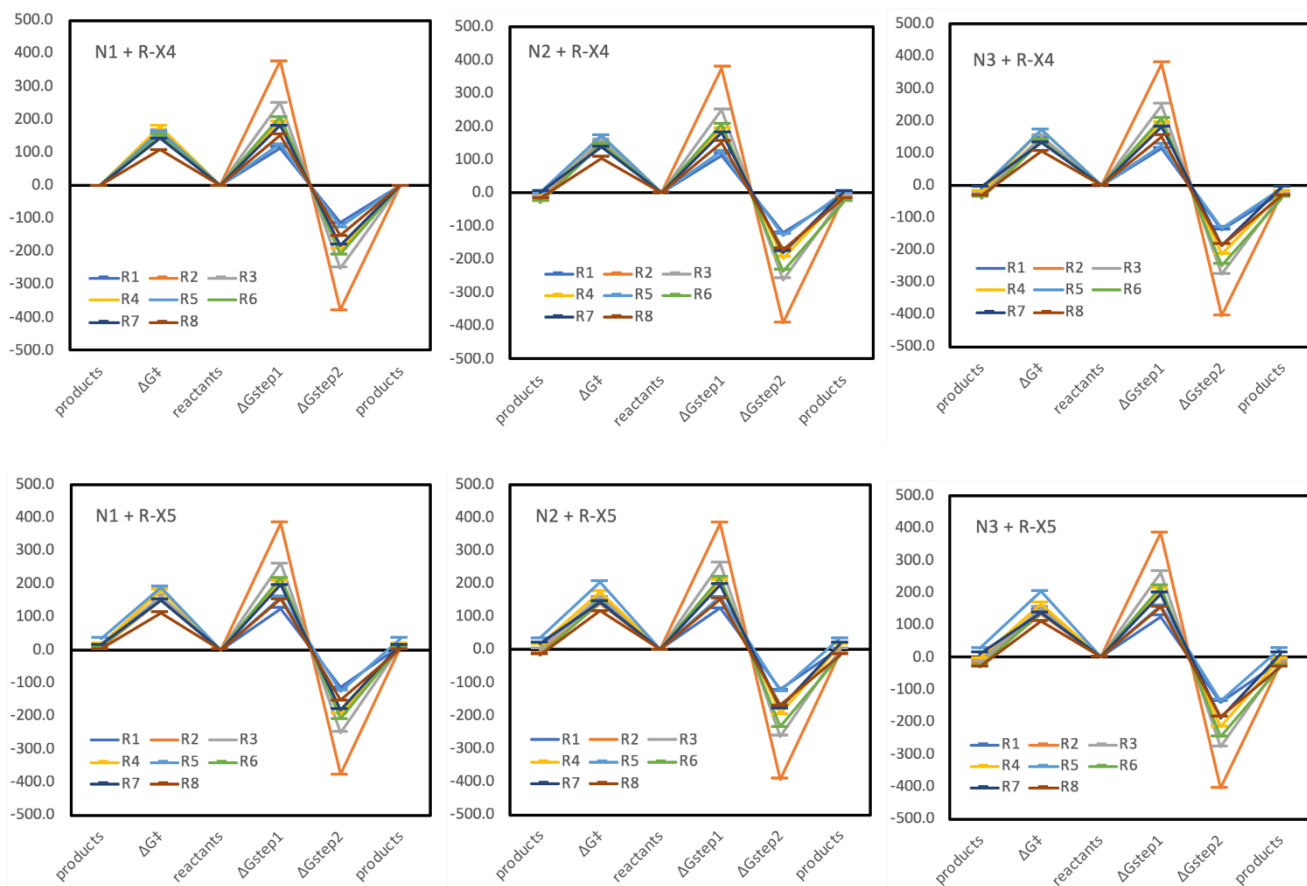
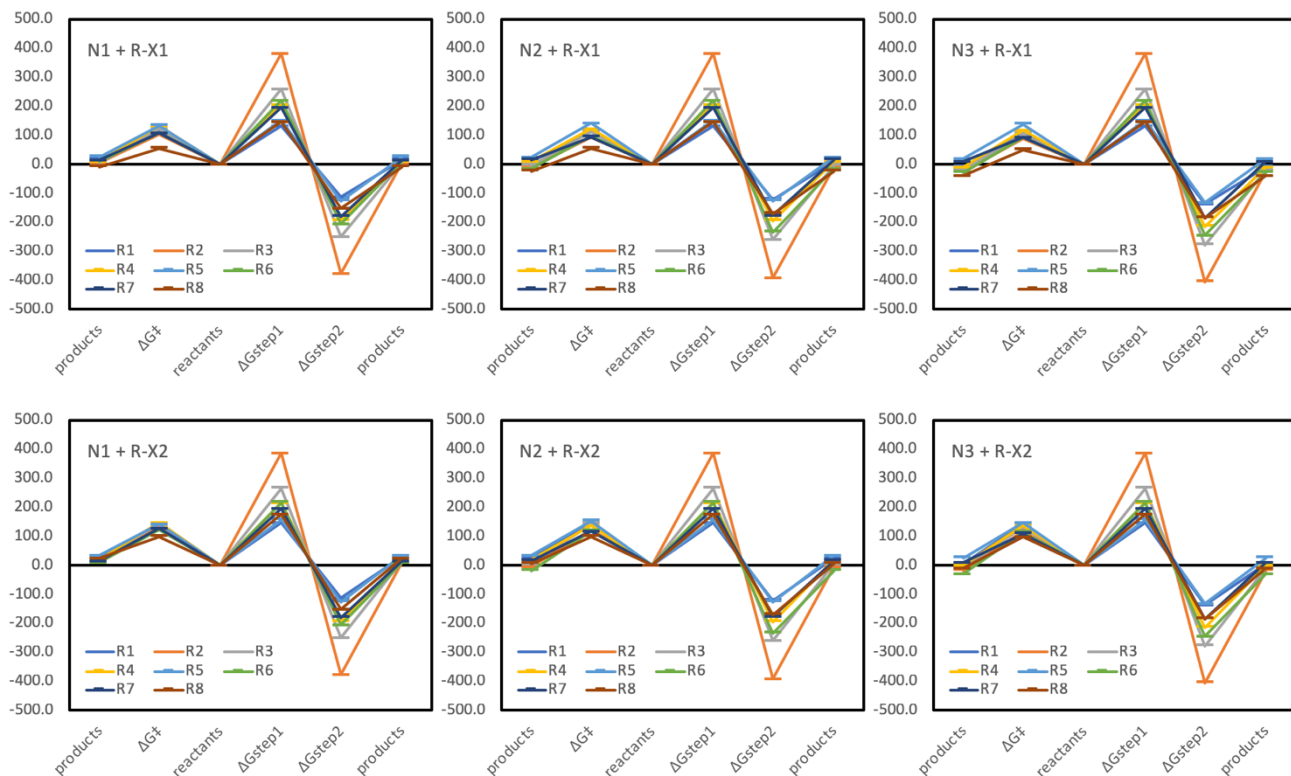


Figure 4 Gibbs free energy surfaces (kJ mol^{-1} 298.15K, dichloromethane) showing competing $\text{S}_{\text{N}}2$ (LHS of each plot) and $\text{S}_{\text{N}}1$ (RHS) processes as a function of R-group for the Type II reactions involving combinations of neutral nucleophiles N1–N3 and neutral leaving groups X4 and X5. For structures of all species see Scheme 2.



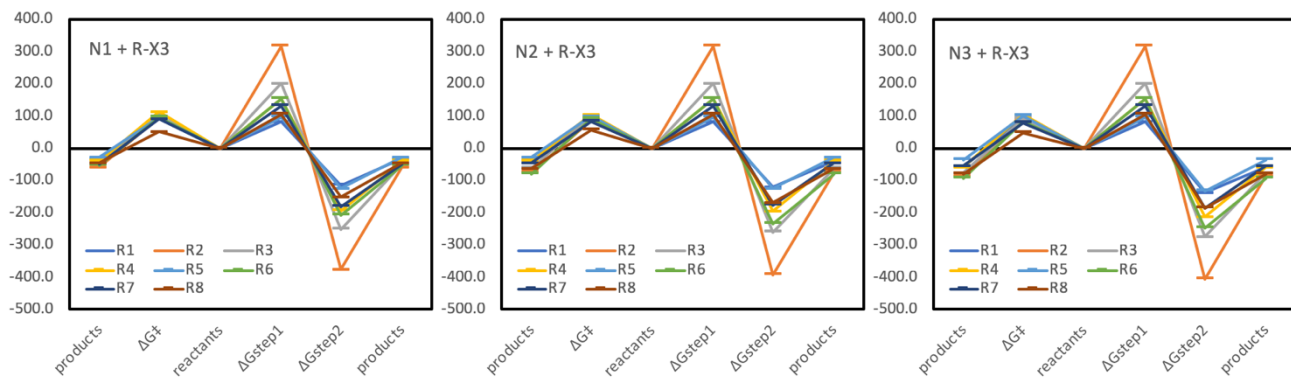


Figure 5. Gibbs free energy surfaces (kJ mol^{-1} 298.15K, dichloromethane) showing competing $\text{S}_{\text{N}}2$ (LHS of each plot) and $\text{S}_{\text{N}}1$ (RHS) processes as a function of R-group for the Type III reactions involving combinations of neutral nucleophiles N1–N3 and anionic leaving groups X1–X3. For structures of all species see Scheme 2.

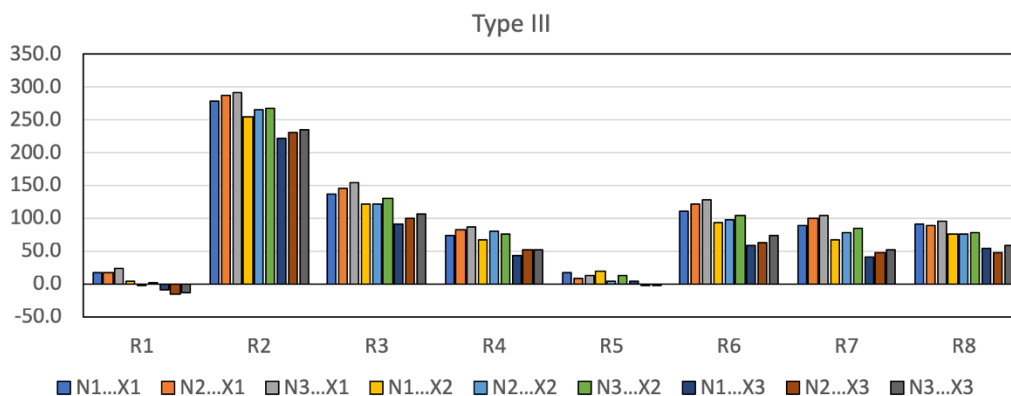
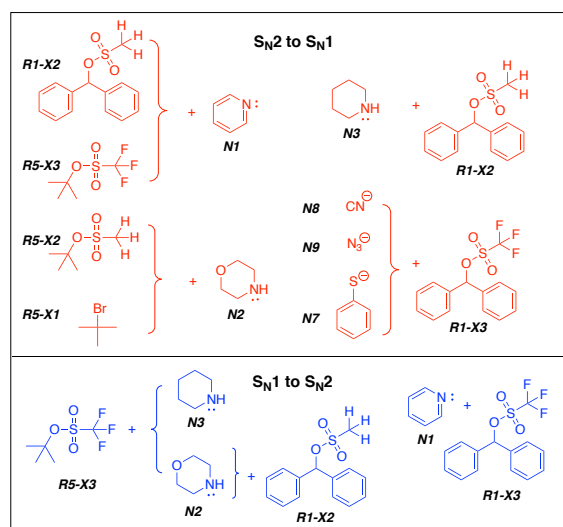


Figure 6. Gibbs free energy differences (kJ mol^{-1} 298.15K, dichloromethane) between the energy bottle necks for $\text{S}_{\text{N}}1$ (step 1 $\square G^\ddagger$) and $\text{S}_{\text{N}}2$ ($\square G^\ddagger$) as a function of R-group for the Type III reactions involving combinations of neutral nucleophiles (N1–N3) and anionic leaving groups (X1–X3). Differences are defined such that a positive number indicates that $\text{S}_{\text{N}}2$ is preferred. For structures of all species see Scheme 2.

Type III reactions. The “Type III” reactions involve the neutral nucleophiles (N1–N3) and charged leaving groups (X1–X3) and have no charge conservation in either the $\text{S}_{\text{N}}2$ or competing $\text{S}_{\text{N}}1$ steps. As such neither process is expected to be particularly favorable but some cancellation from the $\text{S}_{\text{N}}2$ transition state (i.e., because full charge separation has not yet occurred) should favor it in general, which is indeed the case (Figure 5). However, as with the other systems, the $\text{S}_{\text{N}}1$ favorability increases with carbocation stability and electron donating ability as expected with the highly stabilized carbocations R1 and R5 showing $\text{S}_{\text{N}}1$ preferences for some combinations of nucleophiles and leaving groups (Figure 6). The best candidates for $\text{S}_{\text{N}}1$ / $\text{S}_{\text{N}}2$ switching would involve these cations with the various combinations of leaving groups and nucleophiles studied.

Electrostatic Switching. Scheme 3 summarizes the best candidates for electrostatic switching between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ of the test set of 264 reactions studied. The 12 reactions shown have $\text{S}_{\text{N}}1$ / $\text{S}_{\text{N}}2$ differences within $\pm 10 \text{ kJ mol}^{-1}$. To test the effect of electric field, we selected a pair of reactions with approximately equal and opposite $\text{S}_{\text{N}}1$ / $\text{S}_{\text{N}}2$ preferences and involving a common substrate (Figure 7). We then placed positive and negative point charges near the para-position of the nucleophile to approximately line up with the reaction axis and calculated the new $\text{S}_{\text{N}}2$ barriers, and hence the new $\text{S}_{\text{N}}1$ to $\text{S}_{\text{N}}2$ preferences (Table S7). As a mimic of a more practical system we also placed COOH and NMe₂ in the para-position and

calculated the barriers in the charged and neutral forms (Table S7). For the pyridine nucleophile (N1), an extra CH₂ spacer was included before the charged group to prevent π -conjugation with the reaction center.



Scheme 3. Reactions where the $\text{S}_{\text{N}}1$ / $\text{S}_{\text{N}}2$ preferences are within $\pm 10 \text{ kJ mol}^{-1}$. Red indicates $\text{S}_{\text{N}}2$ is preferred and blue indicates $\text{S}_{\text{N}}1$ is preferred.

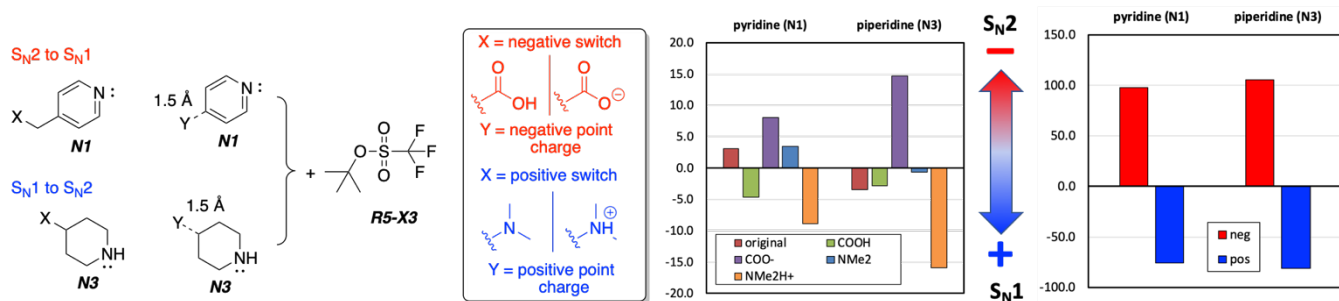


Figure 7. The effect of charged functional groups and point charges on nucleophilic substitution. The left-hand-side chart shows the difference in the energy bottle necks for S_N1 versus S_N2 , calculated as a Gibbs free energy difference (kJ mol^{-1}) at 298.15 K for the neutral and charged functional groups in dichloromethane. The right-hand-side chart assesses the effect of point charges on this preference using gas-phase electronic energies on the same (dichloromethane optimized) geometries. A positive number indicates that S_N2 is preferred.

From Figure 7, it is clear that a negative charge on the nucleophile side of the S_N2 transition state relatively favors the S_N2 process by stabilizing the developing positive charge on the $N-R^+$ product. Conversely, a positive charge in the same position favors S_N1 by destabilizing this developing positive charge. When the charged functional group is used in place of a point charge, the same general trends are seen, but there the effects are much smaller. This is due to a number of factors, the most significant being the use of gas-phase electronic energies to estimate the point charge effects on the S_N2 barriers. The effects in dichloromethane would be much smaller due to dielectric screening, but computing reactions with point charges in a dielectric continuum is not meaningful. Other differences arise because the point charge is less diffuse,²⁹ and from non-electrostatic effects from the charged-functional group. These latter effects can be seen by comparing the neutral species (original, COOH and NMe₂) which are not identical. Unsurprisingly the differences among these three neutral systems are larger for the pyridine (N1) reactions as here the CH₂ spacer group breaks π -conjugation but not hyperconjugation. Nonetheless it is clear from the point charge results that electrostatic effects are primarily responsible for S_N2 to S_N1 and S_N1 to S_N2 switching.

CONCLUSIONS

Nucleophilic substitution can proceed via S_N1 or S_N2 mechanisms according well-known factors such as the charge on the nucleophile and leaving group, their stabilities and the stability of the carbon cation intermediate. In this work we show that these inherent preferences can be subverted by external electric fields or the electrostatic effect of charged functional groups. The best reactions for observing this change in preference are those involving neutral nucleophiles and anionic leaving groups, for which a positive charge on the nucleophile side favors S_N1 and a negative charge favors S_N2 . While these trends are intuitive, the significant conclusion is that practically accessible electrostatic effects are large enough to reverse reaction preferences for the suggested case studies presented.

ASSOCIATED CONTENT

Supporting Information

Numbers used to make all of the charts, data in different solvent environments, and geometries and total energies in the form of Gaussian archive entries. The Supporting Information is available free of charge on the ACS Publications website.

Corresponding Author

* Email: michelle.coote@anu.edu.au

Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

The authors acknowledge an Australian Research Council (ARC) Laureate Fellowship (to M.L.C.), and generous allocations of supercomputing time from the National Computational Infrastructure

Funding Sources

Australian Research Council (FL170100041, CE140100012)

REFERENCES

- Shaik, S.; Mandal, D.; Ramanan, R. Oriented Electric Fields As Future Smart Reagents In Chemistry. *Nat. Chem.* 2016, 8, 1091–1098.
- Shaik, S.; Ramanan, R.; Danovich, D.; Mandal, D. Structure And Reactivity/Selectivity Control By Oriented-External Electric Fields. *Chem. Soc. Rev.* 2018, 47, 5125–5145.
- Ciampi, S.; Darwish, N.; Aitken, H. M.; Díez-Pérez, I.; Coote, M. L. Harnessing Electrostatic Catalysis In Single Molecule, Electrochemical And Chemical Systems: A Rapidly Growing Experimental Tool Box. *Chem. Soc. Rev.* 2018, 47, 5146–5164.
- Aragonès, A. C.; Haworth, N. L.; Darwish, N.; Ciampi, S.; Bloomfield, N. J.; Wallace, G. G.; Díez-Pérez, I.; Coote, M. L. Electrostatic Catalysis Of A Diels-Alder Reaction. *Nature* 2016, 531, 88–91.
- Zhang, L.; Laborda, E.; Darwish, N.; Noble, B. B.; Tyrell, J. H.; Pluczyk, S.; Le Brun, A. P.; Wallace, G. G.; Gonzalez, J.; Coote, M. L.; Ciampi, S. Electrochemical And Electrostatic Cleavage Of Alkoxyamines. *J. Am. Chem. Soc.* 2018, 140, 766–774.
- Akamatsu, M.; Sakai, N.; Matile, S. Electric-Field-Assisted Anion-II Catalysis. *J. Am. Chem. Soc.* 2017, 139, 6558–6561.

7. Gorin, C. F.; Beh, E. S.; Kanan, M. W. An Electric Field-Induced Change In The Selectivity Of A Metal Oxide-Catalyzed Epoxide Rearrangement. *J. Am. Chem. Soc.* 2012, 134, 186–189.
8. Gryn'ova, G.; Marshall, D. L.; Blanksby, S. J.; Coote, M. L. Switching Radical Stability By pH-Induced Orbital Conversion. *Nat. Chem.* 2013, 5, 474–481.
9. Klinska, M.; Smith, L. M.; Gryn'ova, G.; Banwell, M. G.; Coote, M. L. Experimental Demonstration Of pH-Dependent Electrostatic Catalysis Of Radical Reactions. *Chem. Sci.* 2015, 6, 5623–5627.
10. Gryn'ova, G.; Smith, L.M.; Coote, M.L. Computational Design Of pH-Switchable Control Agents For Nitroxide Mediated Polymerization *Phys. Chem. Chem. Phys.*, 2017, 19, 22678-22683.
11. Jiang, J. Y.; Smith, L. M.; Tyrell, J. H.; Coote, M. L. Pulsed Laser Polymerisation Studies Of Methyl Methacrylate In The Presence Of $AlCl_3$ and $ZnCl_2$ -Evidence Of Propagation Catalysis. *Polym. Chem.* 2017, 8, 5948–5953.
12. Yue, L.; Wang, N.; Zhou, S.; Sun, X.; Schlangen, M.; Schwarz, H. The Electric Field As A “Smart” Ligand In Controlling The Thermal Activation Of Methane And Molecular Hydrogen. *Angew. Chemie Int. Ed.* 2018, 57, 14635-14639.
13. Brak K.; Jacobsen, E. N., Asymmetric Ion-Pairing Catalysis, *Angew. Chem. Int. Ed.* 2013, 52, 534 – 561
14. Bhattacharyya, K.; Karmakar S.; Datta A., External Electric Field Control: Driving The Reactivity Of Metal-Free Azide–Alkyne Click Reactions *Phys. Chem. Chem. Phys.*, 2017, 19, 22482-22486.
15. Che, F.; Gray, J.T.; Ha, S.; Kruse, N.; Scott, S.L.; McEwen, J.-S., Elucidating The Roles Of Electric Fields In Catalysis: A Perspective, *ACS Catal.* 2018, 8, 5153–5174.
16. Meir, R.; Chen, H.; Lai, W.; Shaik, S. Oriented Electric Fields Accelerate Diels-Alder Reactions And Control The Endo/Exo Selectivity. *Chemphyschem* 2010, 11, 301–310.
17. Wang, Z.; Danovich, D.; Ramanan, R.; Shaik, S., Oriented-External Electric Fields Create Absolute Enantioselectivity In Diels–Alder Reactions: Importance Of The Molecular Dipole Moment *J. Am. Chem. Soc.*, 2018, 140, 13350–13359
18. Aitken, H. M.; Coote, M. L. Can Electrostatic Catalysis Of Diels-Alder Reactions Be Harnessed With pH-Switchable Charged Functional Groups? *Phys. Chem. Chem. Phys.* 2018, 20, 10671–10676.
19. Hill, N.S.; Coote, M.L., Internal Oriented Electric Fields As A Strategy For Selectively Modifying Photochemical Reactivity *J. Am. Chem. Soc.* 2018 DOI: 10.1021/Jacs.8b12009.
20. Shaik, S.S.; Pross, A., S_N2 Reactivity Of CH_3X Derivatives. A Valence Bond Approach *J. Am. Chem. Soc.* 1982, 104, 2708-2719.
21. Ramanan, R. ; Danovich, D.; Mandal, D.; Shaik, S., Catalysis Of Methyl Transfer Reactions By Oriented External Electric Fields: Are Gold–Thiolate Linkers Innocent? *J. Am. Chem. Soc.* 2018, 140, 4354–4362
22. Menschutkin, N. Über Die Affinitätskoeffizientender Alkylhaloide Und Der Amine *Z. Phys. Chem.* 1890, 6, 41.
23. Shaik, S.; Shurki, A., Valence Bond Diagrams And Chemical Reactivity *Angew. Chem. Int. Ed.* 1999, 38, 586-625
24. Katrizky, A.R.; Brycki, B.E., The Mechanisms Of Nucleophilic Substitution In Aliphatic Compounds *Chem. Soc. Rev.* 1990, 19, 83-10520
25. Alecu, I.; Zheng, J.; Zhao, Y.; Truhlar, D. G. Computational Thermochemistry: Scale Factor Databases And Scale Factors For Vibrational Frequencies Obtained From Electronic Model Chemistries *J. Chem. Theory Comput.* 2010, 6, 2872–2887
26. Ribeiro, R. F.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Use Of Solution-Phase Vibrational Frequencies In Continuum Models For The Free Energy Of Solvation. *J. Phys. Chem. B* 2011, 115, 14556–14562.
27. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based On Solute Electron Density And A Continuum Model Of The Solvent Defined By The Bulk Dielectric Constant And Atomic Surface Tensions. *J. Phys. Chem. B.* 2009, 113, 6378–6396.
28. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Et Al., Gaussian 09, Revision E.01. Gaussian, Inc.: Wallingford CT 2016.
29. Gryn'ova G., Coote M.L. Origin And Scope Of Long-Range Stabilizing Interactions And Associated SOMO-HOMO Conversion In Distonic Radical Anions *J. Am. Chem. Soc.* 2013, 135, 15392-15403.

