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Mechanism of Base-Catalyzed Halogen Dance Reactions and the Role of Bromo-Bridged Transition States

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Abstract:

Base-catalyzed halogen dance reaction, has puzzled chemists ever since, to come up with new ideas regarding the mechanism of this beautiful chemical transformation. Series of fast metal-halogen exchanges are among the most recent mechanisms. Using DFT-Cam-B3LYP/ land2dz computations and focused on Halogen Dance (HD) reactions of bromobenzene derivatives, new bromo-bridged Transition States (TS) are proposed. These are then used to lay out 8 possible isomerization and 18 possible disproportionation paths. Mechanistic pathways were then analyzed based on TS's energy and protonation/deprotonation steps to find the most suitable pathways. Overall pattern of these mechanisms draws for the first-time a cascade-like pattern for base-catalyzed halogen dance in its entirety. The present work shed light on a dynamic domino mechanism which dominates the realm of nonaqueous strongly basic medium reactions. Trends like these may well be a shared feature in base digestion of wood for its precious poly aromatic component like lignin.

Keywords: mechanistic pathways, dynamic domino mechanisms, base-catalyzed halogen dance, nonaqueous strongly basic medium, bromo-bridged Transition State, disproportionation paths.

Introduction:

Aryl halide reactions in strong basic medium has tasked the minds of such great chemists like Chichibain and Bunnet. Yet to fully address chemistry of anions one should add the role of strong nonaqueous basic media[1-2] the niches of which still invites those who dare to step into uncharted territories. Aryl halides reactions in basic media has appeared in literature with different names like halogen scrambling, halogen migration[3], halogen isomerization, halogen dance, or base catalyzed halogen dance[4-6], which implies the lack of a consensus for the underpinning mechanism.

In 1971 Joseph F. Bunnet et al., published an insightful paper [4]on the so-called base catalyzed halogen dance reaction. [7-8] The report not only, revolutionized our understanding of the reaction, but also ruled out then accepted benzyne mechanism and has tagged the name *base catalyzed Halogen dance* to this efficient synthetically versatile reaction so far. Hereafter the halogen dance (HD) reaction is used. In this paper we try to purpose a mechanism that can explain the so-called HD reactions in great detail for the first time, and that is the pseudo nucleophilic attack on a halogen electrophilic center also recently referred to as SN@X [9] mechanism.

Joseph F. Bunnet points out [4] the sluggish reactivity of aryl halides as mentioned in organic chemistry textbooks back then. And among the more advanced reaction mechanisms, he points out Substitution Nucleophilic Aromatic, SNAr, mechanism which includes Aryl lithium compounds. He also correctly predicts the domain of aryl halide reactions to be much more versatile. But even today, at a time when these reactions are being exploited by synthetic chemists the reaction is largely realized as *a cascade of deprotonation (metal–hydrogen exchange) and metal–halogen exchange reactions ultimately leading to the most stable organometal species*[10]. However, to this chaotic maze of halogen metal exchanges etc.…, there is order and to explain it is the main purpose of this work.

Computational Methods:

All computations were done at DFT-Cam-B3LYP/ lanl2dz level of theory[11-17], using gaussian g09 package[18-20], the reliability of basis set is already proven to yield very similar to results obtained with CCSDT coupled cluster configurational methods[21-26], in particular for halogens and their long-range contact be it of parallel or orthogonal X---X interactions. The choice of DFT-Cam-B3LYP/ lanl2dz level of theory is mainly based on the reliable reproducible TS structures that are consistent with regard to the dihedral between the two benzene rings in their structure. Bond lengths were in cases slightly corrected at MP2/aug cc-pVTZ level of theory. Frequency computations were done for all TS structures to estimate the smoothness and dynamics of the TS formation (ongoing research in this part as to address issues on Tunneling and quantum mechanical QM charge transfer CT effects in TS complexes are in progress and deserve a separate assessment and report when completed). To further evaluate the role of HOMO-LUMO gaps[27-28] in resonance and polarizability, electronic structures of conjugate anions of some derivatives were also geometry optimized . In many of the mechanistic cycles' directionality is judged based on the basicity and nucleophilicity double checked via polarizabilities as well. The latter confirmed reliability of geometries regarding the reported C-H bond lengths in table 1. The C-Br bond lengths though show slight changes but are a perfect measure as to address the electrophilicity of bromine centers, again due to the promising Cam-B3LYP/ land2dz method and basis set combinations for halogen containing compounds.

Results and discussions:

To discuss the mechanism of HD reactions, its noteworthy to point out to two main reactivity aspects in these reactions, and then move into the jumble of reactions trying to paint the big picture at the end. We would focus on bromobenzene derivatives to make the discussion sharper and more disciplined as well. Firstly, the C-H basicity increases as one moves from benzene to its poly brominated derivatives. Secondly the bromine substituents become more and more electrophilic through poly bromination. Such electrophilic bromines are now more susceptible to strong nucleophilic attack forming bridged anionic Transition States (TS) as the main mechanistic feature thoroughly explained in this report. The net result of any HD reaction is the transfer of a positive halogen atom. and the main mechanistic push seems to be the same source of that positive halogen. Back in 1971 Bunett et al. noticed that co-solvants like DMSO are capable of accelerating the rate of the reaction, While DMF, with very similar dielectric constant are completely ineffective in rate acceleration of the reaction[4]. They reasonably argued that co-solvants , capable of producing anions, happened to be effective for accelerating HD reactions. Also as recently as 2019 reagents like pentafluoro iodo benzene as well as pentafluoro 2-iodio propane were found extremely helpful as reported by Gronert et al.[29]. Even though there is no direct evidence of free existing positive halogens, reagents like pentafluoro 2-iodio propane and pentafluoro iodo benzene are of pivotal role in the rate equation of halogen dance reactions and the concentration of anions are of partial importance. An ideal candidate for HD reaction is a bromobenzene derivative that poses a good balance towards both deprotonation of H and attack on electrophilic Br as well. Such candidates however, are neither the penta brominated nor mono brominated derivatives, but the specially substituted cases where two traits can be maximally or minimally manifested. One such case is the 1,2,4 tribromobenzene derivative with both H acidity and Br electrophilicity and enough stability to make it more of an autocatalytic nature, feeding the frenzied dance of halogens in these reactions. The Autocatalytic activity pointed out by Bunnet et al. can also be rooted out in the delicate balance between H acidity and Br electrophilicity.

As the C-H bong becomes shorter, acidity increases making the conjugate anion more stable. Also a smaller C-Br would imply more resonance interaction between the bromine and the aromatic system (this more extensive resonance is reflected in smaller HOMO-LUMO gaps), which makes the Bromine center more susceptible to electrophilic attack. These trends are all listed in table 1 for bromobenzene derivatives along with their relative energies. It's important to note that energies are reported as the sum of CH and CBr units in each derivative with reference to the most stable CH/CBr units. To compare the energies of both reactant, products as well as transition states; monobromobenzene, pentabromobenzene and 1,3,5 tribromobenzene were taken as stability reference compounds each with some CH/CBr units. So monobromobenzene, pentabromobenzene and 1,3,5 tribromobenzene were translated into stability equations of X+5Y, 5X+Y and 3X+3Y respectively (with X, Y and Z being equal repeating CH/CBr segments in these bromobenzene derivatives). The result is a stability reference X and Y for CH and CBr units respectively. Using such a scheme not only made energy comparisons among different derivatives possible but also made such energy comparisons meaningful. The same approach is also used for relative energies of TS structures were an extra variable Z was added to account for the bridging bromine structural feature which is just as CH, CBr a common feature in all TS structures.

One main mechanistic feature of the TS structures in relation to parent bromobenzene derivatives is that each TS can break into two bromobenzene derivatives, one at a time. Based on this each bromobenzene derivative is labeled with a letter on every bromine atom that can be a potential electrophilic site to be attacked by anions. Since all bromine centers can be attacked, all Br atoms are given a letter code making them a positive halogen center and a potential target for nucleophilic attack (Figure 1). Each TS can then uniquely be defined by a two-letter code designating the two potential bromobenzene derivatives that it can be broken to (see Figure one central panel).

Table 1: **Properties of bromobenzene derivatives based on their abilities to produce potent amphiphilic anions. Most acidic hydrogens and most electrophilic bromines are listed as well as HOMO-LUMO gap indicating most conjugate systems. (Energies are the comparable between the all derivatives based on the CH/CBr stability feature explained in text)**

Bromobenzene Derivatives	Most Acidic C-H Bond Length (Å)	Most Electrophilic C-Br Bond Length (Å)	HOMO-LUMO Gap (eV)	E rel(kcal)
Mono	1.085	1.947	9.05	5.9
Ortho	1.085	1.945	8.70	5.1
Para	1.084	1.950	8.50	2.6
Meta	1.084	1.951	8.69	2.7
1,2,3 tri	1.084	1.937	8.37	5.5
1,2,4 tri	1.084	1.941	8.40	2.4
1,3,5 tri	1.084	1.947	8.67	0.4
1,2,3,5 tetra	1.083	1.943	8.05	3.5
1,2,4,5 tetra	1.084	1.938	8.23	2.6
1,2,3,4 tetra	1.084	1.939	7.91	6.4
1,2,3,4,5 Penta	1.083	1.936	7.64	7.8
hexa	-	1.939	7.34	13.9

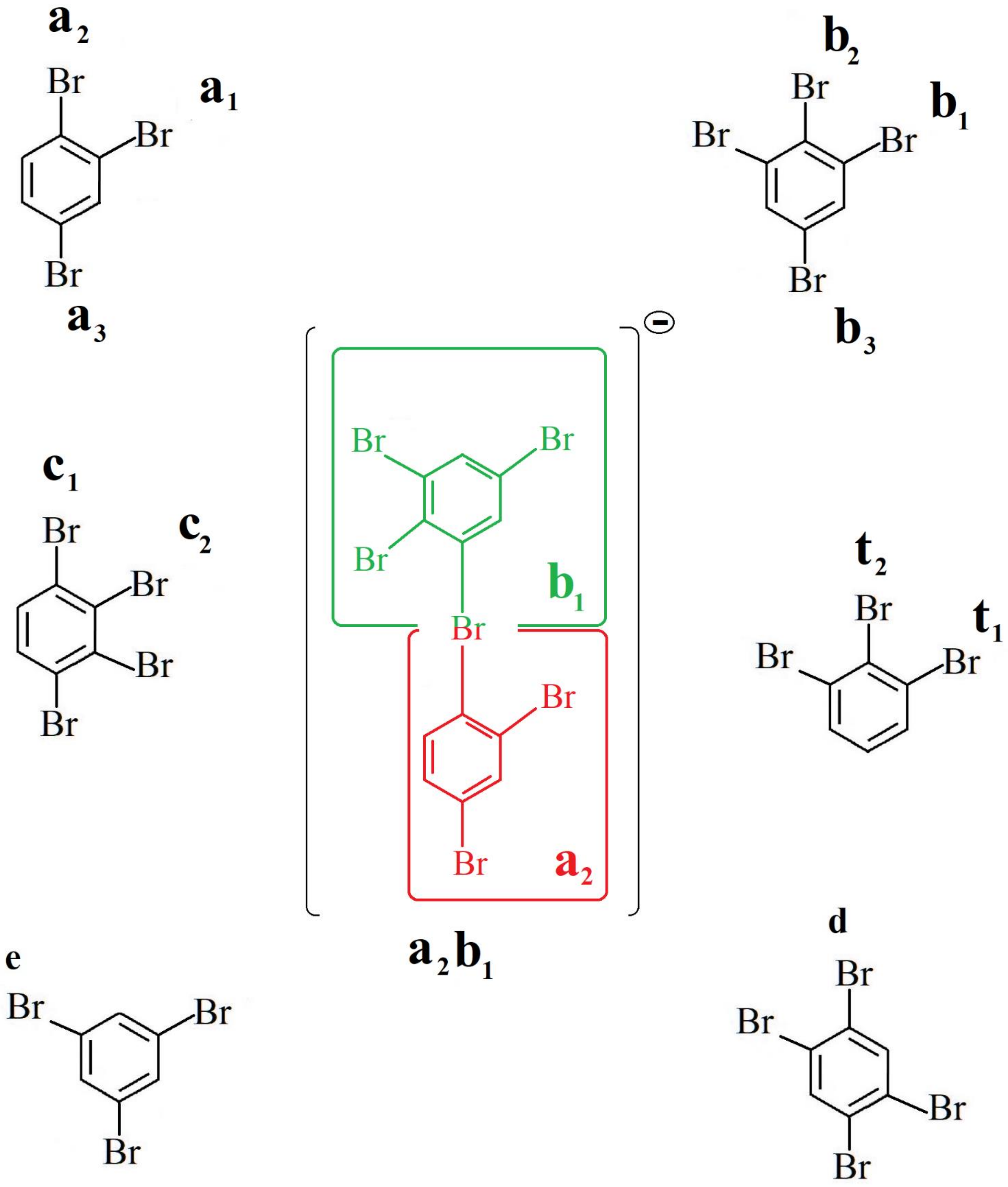

Figure 1: **Donor acceptor moieties of SN@Br Intermediates labeled based on the bridged Bromine atoms. (which can form 46 different TS configurations; only one which is shown at the center here).**

With this brief discussion this report aims to investigate the two aforementioned trends starting with dibromo and tribromo derivatives visiting the famous Bunnet-type reaction. Then it moves onto possible disproportionation reactions including tetrabromo derivatives that are potential sources of positive halogens. These three classes, will then make the bigger pattern stand out of the jumble of HD reactions in bromobenzene derivatives.

The isomeration of dibromobenzene derivative is less noticed in the literature but it can fit well into the realm of HD reactions if a proper catalyst 1,2,4 tribromobenzene ***a*** is present in trace amounts, again as a key source of positive halogen atoms. The reaction mechanism is much like that of a photochemical radical reaction where a single radical can repeat a cycle over a thousand times before quenching. Here the TS and ***a*** are repeatedly used and reproduced while the isomerization reaches completion. The direction of the cycle depends on the basicity and nucleophilicity of the anions at the access points of the cycle. The more basic anion (marked MB) is protonated to form the product while the more nucleophilic anion (marked MN) will attack electrophilic bromines in the catalyst, here ***a***, to make TS and drive the cycle forward. The reactant is deprotonated to form the nucleophilic anion which then enters and isomerizes thru the cycle into the final product. Among tribromobenzene only ***a*** and ***t*** can serve as catalyst and ***t*** can only catalyze the meta-ortho isomerization. TS structures involving ***t*** are all of high energy. Figure 2 shows all the possible cycles with catalyst ***a***, among which only the top two are energetically suitable for a catalytic cycle. These include ortho to para and para to meta isomerization for dibromobenzene derivatives. Energies for TS's as well as some other properties are listed in table 2.

Table 2: **Lower energy bromo-bridged TS structures (17 out of 46 is being listed here higher energy TS's more than 15 kcal where ruled out. The two-letter codes are the ones used in Figure 2 to 4). Some stabilizing factors (like the Br-guides leading to linear pseudo Br_3^- feature) has been listed here as well as one destabilizing factor.**

Bromo bridged TS Structures	Br Bridge length (Å)	Br deviation from center (Å)	Linear Pseudo Br_3^- (Å)	Other Br--Br interactions	Para Br--Br	E_{rel} (kcal)
b_3b_2	4.69	0.66	-	0	14.16	6.3
b_1b_2	4.59	0.41	7.35	0	-	5.4
a_3a_2	4.60	0.39	-	0	14.19	9.4
a_1a_2	4.54	0.13	7.59	0	-	6.1
a_3a_1	4.62	0.45	-	0	-	8.0
a_3b_1	4.66	0.57	-	0	-	7.4
c_2b_1	4.60	0.45	7.31	1	-	7.9
a_1b_1	4.56	0.29	7.52	0	-	5.7
db_1	4.53	0.14	7.50	0	-	7.8
a_3b_3	4.58	0.26	-	0	14.19	14.5
c_1b_3	4.57	0.31	-	0	14.10	15.8
a_1b_3	4.56	0.23	-	0	-	10.3
db_3	4.59	0.35	-	0	14.16	11.4
c_1b_1	4.54	0.18	-	1	-	12.5
c_2b_3	4.71	0.69	-	0	-	8.7
t_1b_1	4.57	0.32	7.47	0	-	9.1
t_1b_3	4.55	0.17	-	0	-	14.2

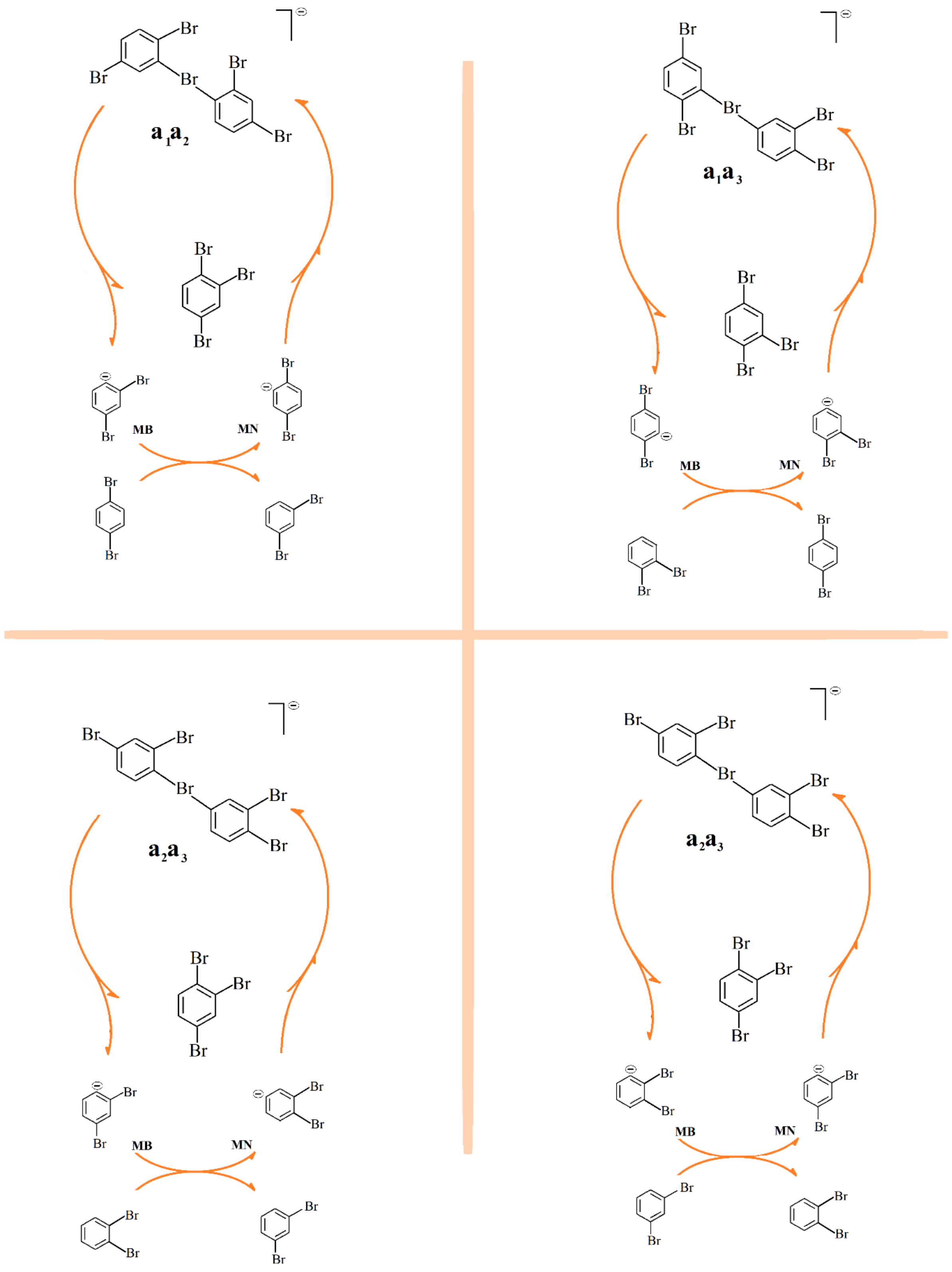

Figure 2: **Possible dibromo isomerization pathways via SN@Br mechanism, for dibromo benzene derivatives.**

For tribromobenzene derivatives, tetrabromobenzenes can serves as catalyst among which ***b*** is the most structurally versatile derivative capable of forming energetically favorable TS structures. One structural possibility with ***c*** is also given here though it forms a high energy TS. However, with ***d*** lack of structural versatility and high energy TS's add up to eliminate any possible mechanistic pathway.

As can be clearly seen energetically favorable isomerizations are ***t*** to ***e*** and ***a*** to ***e*** as well, with the former being more favorable. Among these isomerizations the famous Bunnet type HD reaction is presented as well (Figure 3 top right corner), with ***b*** being the only tribromobenzene with autocatalytic activity for reasons mentioned (even more than ***a*** among dibromobenzene derivatives). And one can clearly see that ***e*** acts as a sink for HD reaction in tribromobenzene derivatives. Figure 3 shows all the possible cycles for isomerization of tribromobenzene derivatives. Again, energies of TS's as well as some other properties are all listed in table 2.

AS mentioned in the beginning neither penta brominated nor mono brominated derivatives are among the ideal candidate in driving the catalytic cycle in HD reactions. However, we have so far identified two potent such candidates in dibromobenzene and tribromobenzene derivatives (***a*** and ***b***). And looking at terabromobenzens at least 18 possible pathways can be found that use a dibromobenzene and a terabromobenzens to yield two tribromobenzenes. These disproportionation reactions are the last link in the chain to reveal the full pattern of HD reactions in bromobenzene derivatives. While only three of the most energetically favorable cycles are provided here (Figure 4). Interested readers can refer to SI for a full account on all 18 possible pathways (see SI). Considering the disproportionation pathways, the evident product of them is the catalytically active kinetically stable 1,2,4 tribromobenzene, which also serves as kind of a lynchpin around which the frenzied halogen dance reactions took place.

Before moving on to the full pattern however, some structural features of TS structures are also worth more elaborate attention. The first feature is the donor acceptor distance, DAD, in the bromo bridged intermediate, and with it the deviation of bridging Br from the exact center. While comments of Br tunneling in these species are only reported for electron transfer reactions there seems to be a clear relation of DAD and energy. This relation generally means an ideal DAD can be found as shorter and shorter contacts are reached and then a sharp rise is observed after a limit. The deviation from the center is also intuitive, there is a more deviation when C-Br strength is greatly different in both sides. Thus, one evident pattern of these HD reactions is their reversibility and that no prefect completion can be reached. Three Br---Br interactions are also considered here. One very stabilizing feature appears to be a linear alignment of two Br on both ends with the central bridging Br to form a pseudo Br_3^- linear substructure that seems to stabilize the TS to a great extent. Other Br---Br interactions of orthogonal or at least nonlinear nature seems to be almost absent in the TS structures, and finally a long-range para-para (both in relation to bridging Br atom) interaction is observed as somewhat of a destabilizing factor in TS studied. The number of TS structures are more than listed here and ongoing research is in progress to fully analyze all the data in order to fully understand these TS structures and their dynamics.

In the big pattern of HD reactions of bromobenzene derivatives (Figure 5) the dibromobenzene isomerizations present two upstream reactions, one to produce para derivative and a quenching branch producing meta derivative as well. There are two downstream reactions with tribromobenzene isomerizations both draining the cascade to the stable 1,3,5 tribromobenzene , ***e***, derivative that plays the role of a chemical sink in HD reactions. The most diverse and multi pathway mainstream of the cascade is formed by three low energy disproportionation reactions with the effective ***b*** as the catalyst in their reaction cycles. Two of the most stable computed TS structures also shown here in Figure 6. Not all of these TS structures are kinetically formed based on H-acidity and Br-electrophilicity. The energy profile for each class of these isomerization and disproportionation reactions, one of the lowest energy pathways are given in Figure 7

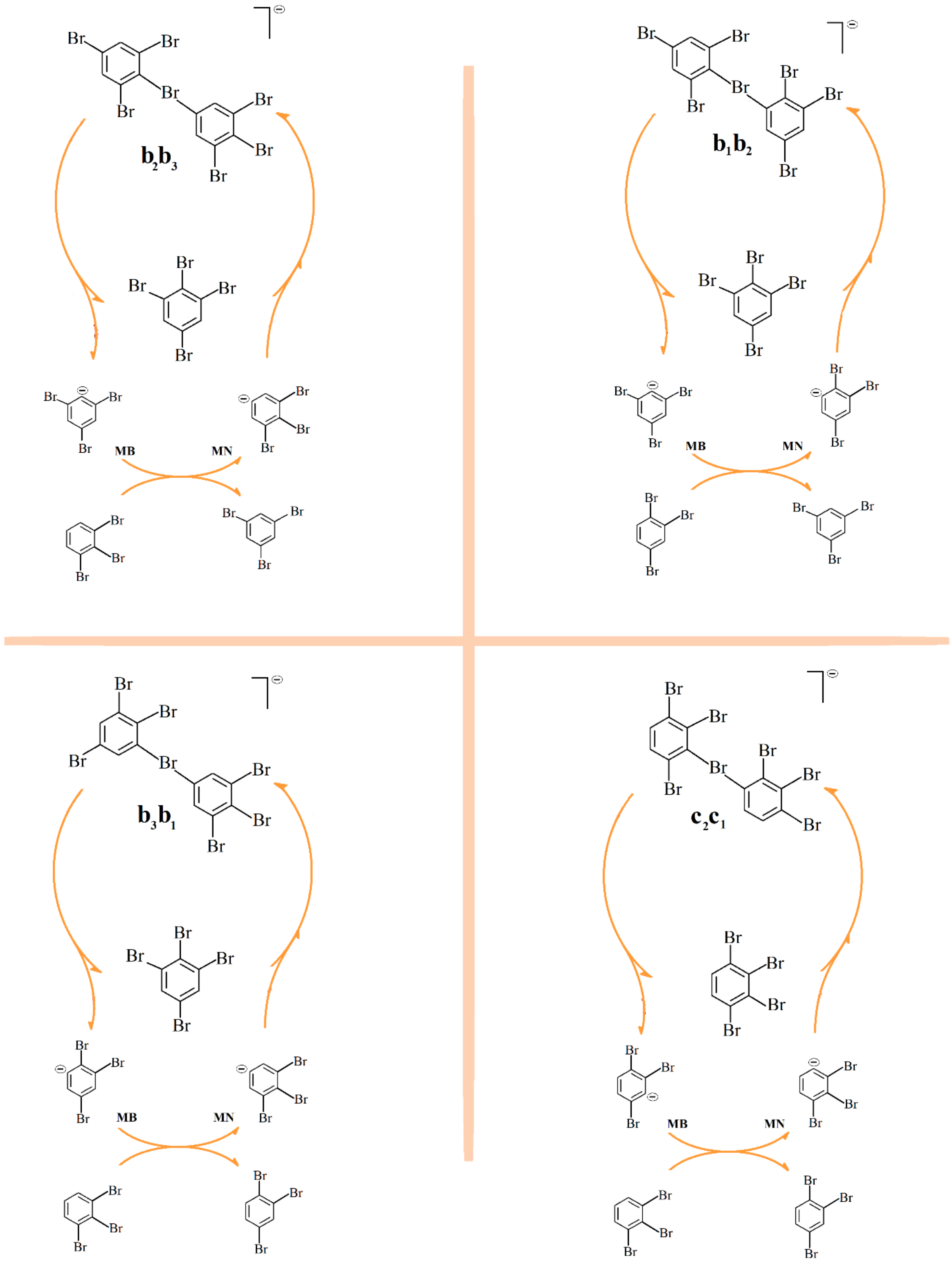

Figure 3: **Possible tribromo isomerization pathways via SN@Br mechanism for tribromo benzene derivatives, including the famous Bunnett type base catalyzed halogen dance reported in 1971.**

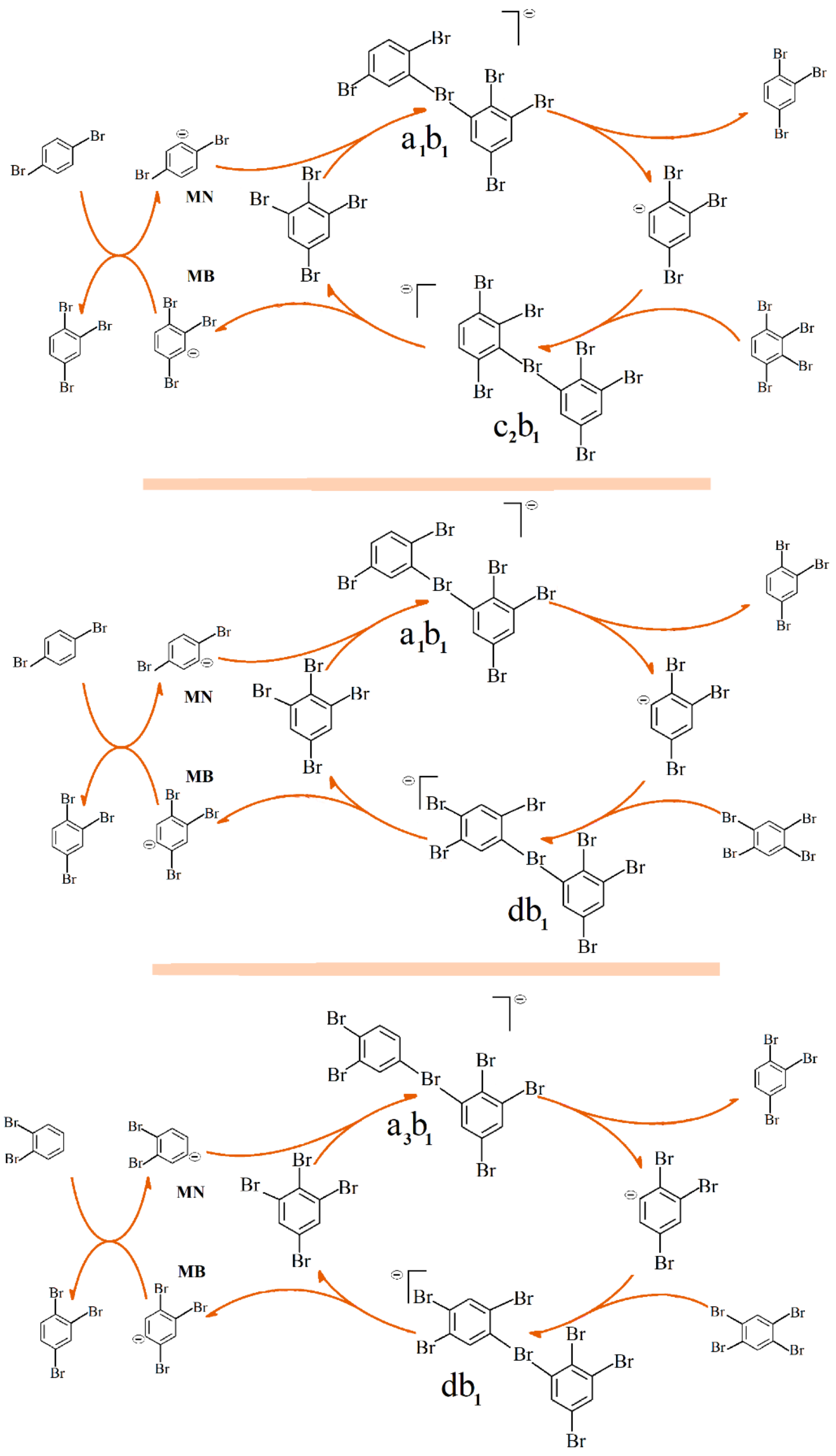

Figure 4: **Three most energetically favorable SN@Br pathways for disproportion of di/tetra bromobenzene derivatives yielding two tribromobenzene products.**

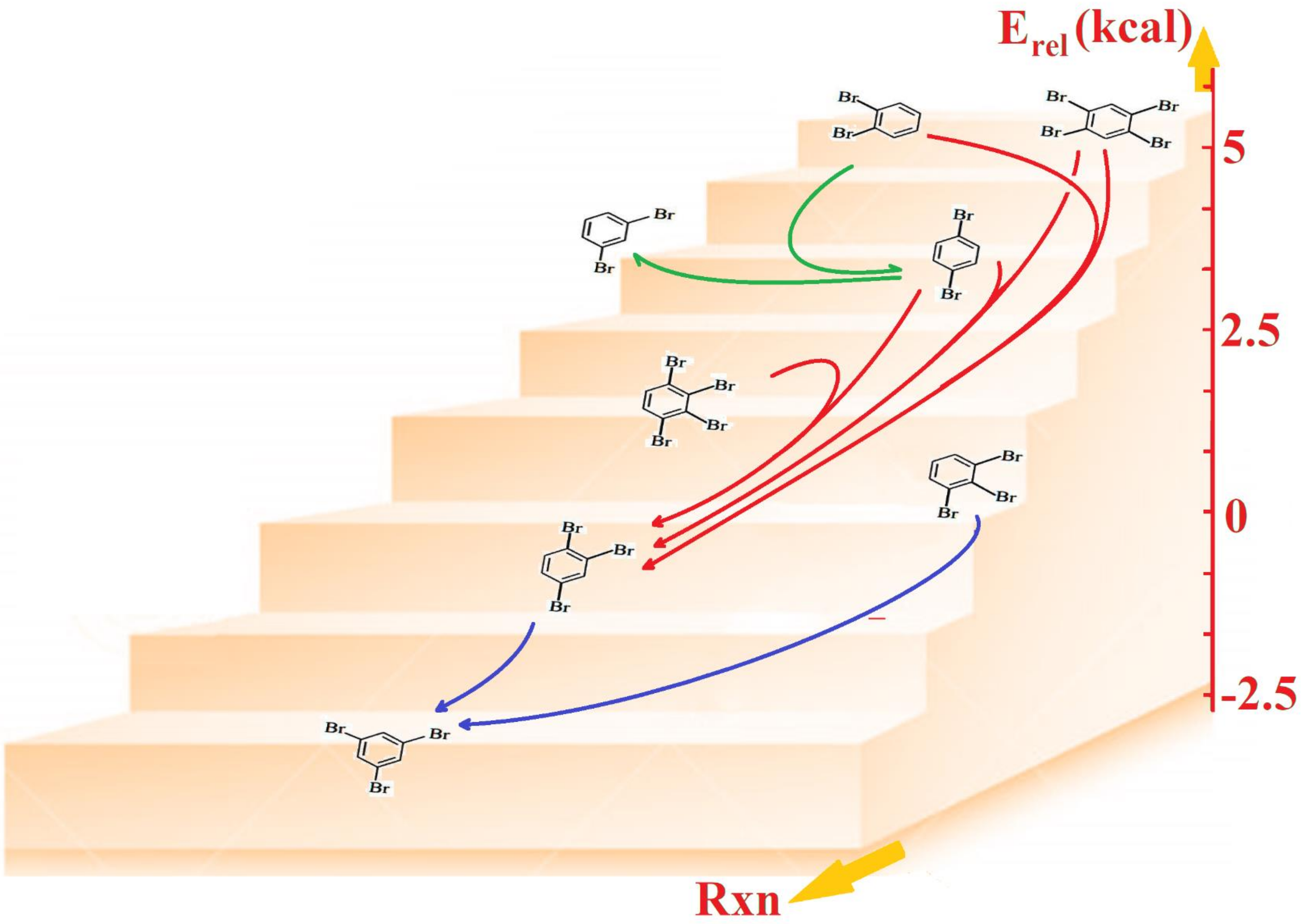

Figure 5: The cascade-like overall Halogen dance reactions in bromobenzene derivatives, with dibromo(green) tribromo(blue) and tetrabromo disproportionation(red) paths along the reaction coordinate.

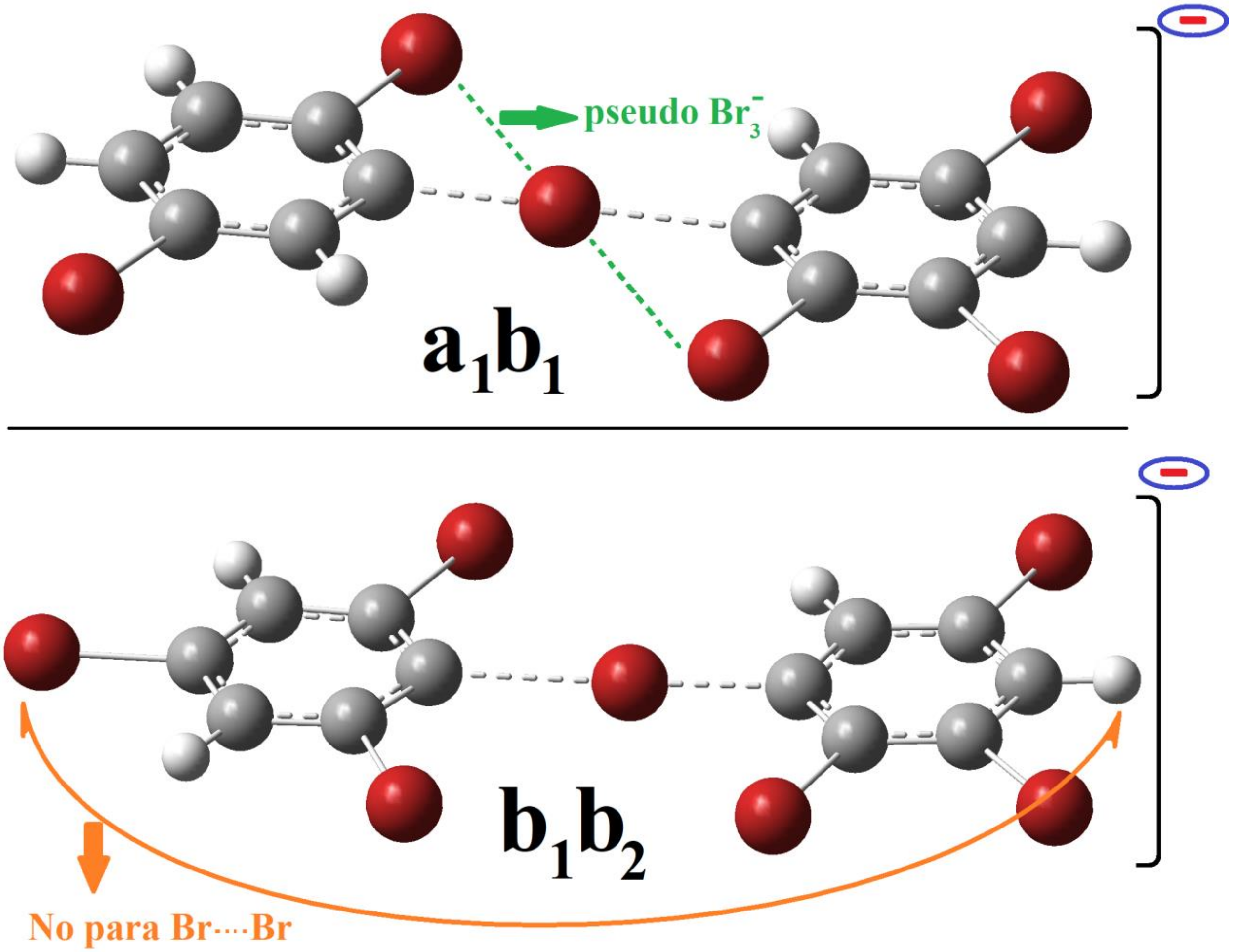

Figure 6: **Two of the most Stable TS structures, some of which are not kinetically formed based on H-acidity and Br-electrophilicity.**

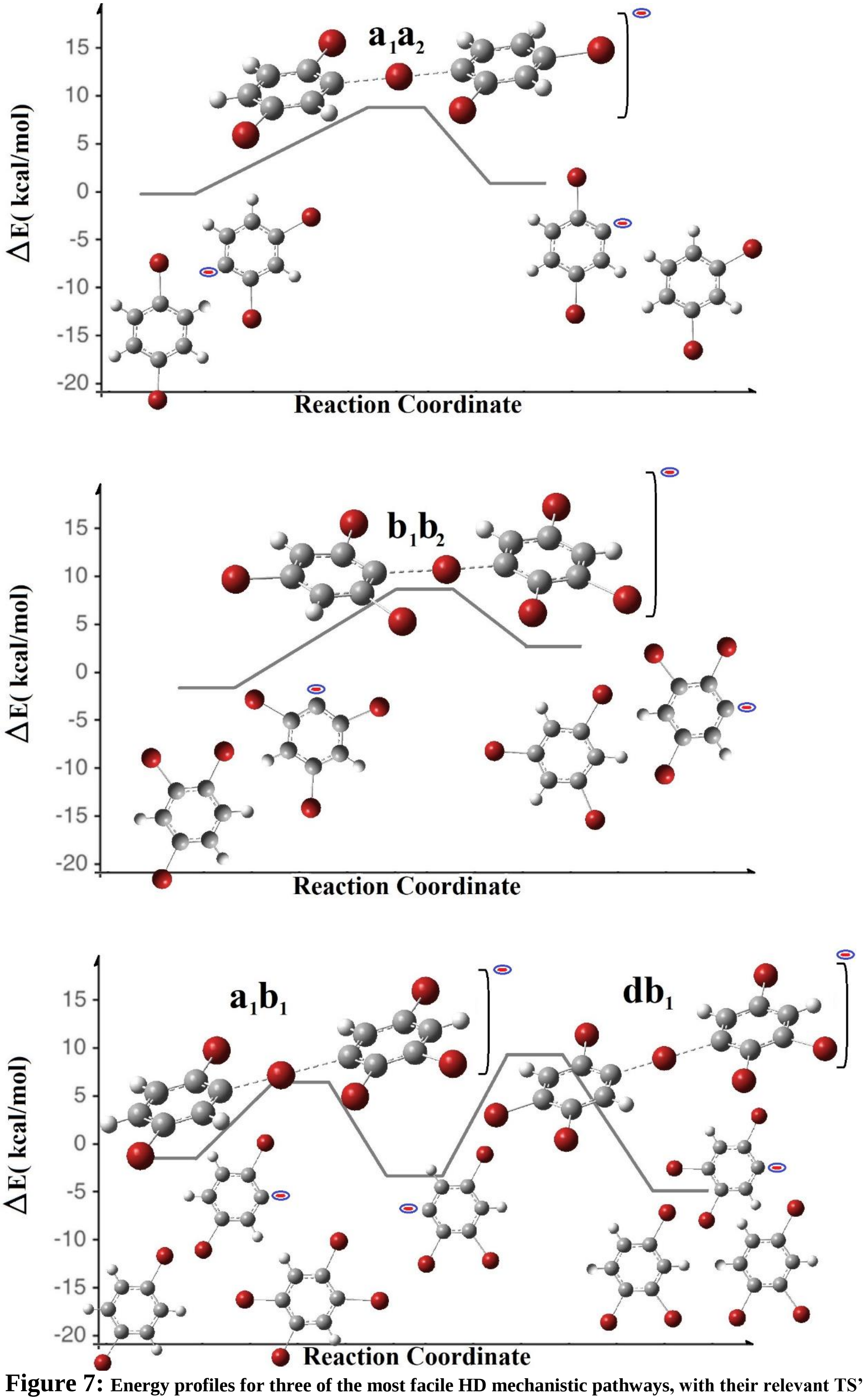

Figure 7: **Energy profiles for three of the most facile HD mechanistic pathways, with their relevant TS's.**

Conclusions:

To summarize the present work tried to present a detailed mechanism of Halogen Dance, HD, reactions in bromobenzene derivatives based on the bromo-bridged transition state, TS, in lieu of all other mechanism. Bromo-bridged transition states can fully explain a cast of HD reactions through energetically favorable mechanistic pathways. The basic concepts that are the main pillars of the suggested mechanism are acidity of Aromatic C-H's and electrophilicity of Br atoms on aryl bromides. A resonance interaction with effects on C-Br bond lengths determines such electrophilic nature. The catalytic cycles not only include all previously reported HD reactions like the famous Bunnet type isomerization but well expand beyond them. The findings also claims a main reason to the puzzling autocatalytic activity of derivatives like 1,2,4 tribromobenzene or 1, 2, 3, 5 terabromobenzens, ***a*** and ***b*** respectively. Such catalytic edge is gained by a delicate balance between H acidity and Br electrophilicity which endows both, ***a*** and ***b*** a kinetic stability as well as their Auto catalytic activity. Features of the TS structures are closely examined and a pseudo Br_3^- linear substructure was found to be a special stabilizing feature. And for the first time a full patterned trend of HD reactions is presented for bromobenzene derivatives. Further studies can illustrate the properties and dynamics of bromo-bridged structures that are shown to be at the heart of halogen dance reactions. Such studies could ultimately pave the path toward a deeper, more detailed understanding of reactions in strong nonaqueous basic media in organic chemistry.

References:

1. Mubarak, M. S.; Peters, D. G., Electrochemical reduction of mono-and dihalothiophenes at carbon cathodes in dimethylformamide. First example of an electrolytically induced halogen dance. *The Journal of organic chemistry* **1996,** *61* (23), 8074-8078.
2. FROHLICH, J., Substituted heterocyclic compounds by selective control of halogen-dance reactions. *Progress in Heterocyclic Chemistry: A Critical Review of the 1993 Literature Preceded by Two Chapters on Current Heterocyclic Topics* **2013,** *6*, 1.
3. Bailey, W. F.; Patricia, J. J., The mechanism of the lithium-halogen interchange reaction: A review of the literature. *Journal of organometallic chemistry* **1988,** *352* (1-2), 1-46.
4. Bunnett, J. F., Base-catalyzed halogen dance, and other reactions of aryl halides. *Accounts of Chemical Research* **1972,** *5* (4), 139-147.

5. Duan, X.-F.; Zhang, Z.-B., Recent progress of halogen-dance reactions in heterocycles. *Heterocycles* **2005,** *65* (8).

6. Schlosser, M., The 2× 3 toolbox of organometallic methods for regiochemically exhaustive functionalization. *Angewandte Chemie International Edition* **2005,** *44* (3), 376-393.

7. Vaitiekunas, A.; Nord, F., Tetrabromothiophene from 2-bromothiophene by means of sodium acetylide in liquid ammonia. *Nature* **1951,** *168* (4281), 875.

8. Vaitiekunas, A.; Nord, F., Studies on the Chemistry of Heterocyclics. XXII. Investigations on the Mechanism of Reactions of 2-Thienyl Halides with Sodium Amide and Sodium Acetylide in Liquid Ammonia. *Journal of the American Chemical Society* **1953,** *75* (7), 1764-1768.

9. Donham, L. L.; Gronert, S., Substitution Reactions on Iodine and Bromine–Mechanisms for Facile Halogenations of Heterocycles. *The Journal of organic chemistry* **2019**.

10. Schnürch, M.; Spina, M.; Khan, A. F.; Mihovilovic, M. D.; Stanetty, P., Halogen dance reactions—A review. *Chemical Society Reviews* **2007,** *36* (7), 1046-1057.

11. Wang, D.; Lü, R.; Yuan, M.; Fu, A.; Chu, T., A DFT/TD-DFT study of thiazolidinedione derivative in dimethylformamide: Cooperative roles of hydrogen bondings, electronic and vibrational spectra. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2014,** *125*, 131-137.

12. Bouzzine, S.; Salgado-Morán, G.; Hamidi, M.; Bouachrine, M.; Pacheco, A. G.; Glossman-Mitnik, D., DFT study of polythiophene energy band gap and substitution effects. *Journal of Chemistry* **2015,** *2015*.

13. Torii, H.; Yoshida, M., Properties of halogen atoms for representing intermolecular electrostatic interactions related to halogen bonding and their substituent effects. *Journal of computational chemistry* **2010,** *31* (1), 107-116.

14. Lu, Y. X.; Zou, J. W.; Fan, J. C.; Zhao, W. N.; Jiang, Y. J.; Yu, Q. S., Ab initio calculations on halogen-bonded complexes and comparison with density functional methods. *Journal of computational chemistry* **2009,** *30* (5), 725-732.

15. Carrera, E. I.; Seferos, D. S., Efficient halogen photoelimination from dibromo, dichloro and difluoro tellurophenes. *Dalton Transactions* **2015,** *44* (5), 2092-2096.

16. Lu, Y.; Zou, J.; Wang, H.; Yu, Q.; Zhang, H.; Jiang, Y., Triangular halogen trimers. A DFT study of the structure, cooperativity, and vibrational properties. *The Journal of Physical Chemistry A* **2005,** *109* (51), 11956-11961.

17. Siiskonen, A.; Priimagi, A., Benchmarking DFT methods with small basis sets for the calculation of halogen-bond strengths. *Journal of molecular modeling* **2017,** *23* (2), 50.

18. Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G., Gaussian 09, revision a. 02, gaussian. *Inc., Wallingford, CT* **2009,** *200*.

19. Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G., Gaussian 09, revision D. 01. Gaussian, Inc., Wallingford CT: 2009.

20. Gaussian, G., 09, Revision A. 02, MJ Frisch, GW Trucks, HB Schlegel, GE Scuseria, MA Robb, JR Cheeseman, G. *Scalmani, V. Barone, B. Mennucci, GA Petersson, H. Nakatsuji, M. Caricato, X. Li, HP Hratchian, AF Izmaylov, J. Bloino and* **2009**.

21. Forni, A.; Pieraccini, S.; Rendine, S.; Gabas, F.; Sironi, M., Halogen-Bonding Interactions with π Systems: CCSD (T), MP2, and DFT Calculations. *ChemPhysChem* **2012,** *13* (18), 4224-4234.

22. Kolar, M. H.; Hobza, P., Computer modeling of halogen bonds and other σ-hole interactions. *Chemical reviews* **2016,** *116* (9), 5155-5187.

23. Mitin, A. V.; van Wüllen, C., Two-component relativistic density-functional calculations of the dimers of the halogens from bromine through element 117 using effective core potential and all-electron methods. *The Journal of chemical physics* **2006,** *124* (6), 064305.

24. Sedlak, R.; Riley, K. E.; Řezáč, J.; Pitoňák, M.; Hobza, P., MP2. 5 and MP2. X: approaching CCSD (T) quality description of noncovalent interaction at the cost of a single CCSD iteration. *ChemPhysChem* **2013,** *14* (4), 698-707.
25. Kato, M.; Hada, M.; Fukuda, R.; Nakatsuji, H., Relativistic configuration interaction and coupled cluster methods using four-component spinors: Magnetic shielding constants of HX and CH3X (X= F, Cl, Br, I). *Chemical physics letters* **2005,** *408* (1-3), 150-156.
26. Liakos, D. G.; Hansen, A.; Neese, F., Weak molecular interactions studied with parallel implementations of the local pair natural orbital coupled pair and coupled cluster methods. *Journal of chemical theory and computation* **2010,** *7* (1), 76-87.
27. Pearson, R. G., Absolute electronegativity and hardness correlated with molecular orbital theory. *Proceedings of the National Academy of Sciences* **1986,** *83* (22), 8440-8441.
28. Duxbury, D. F., The photochemistry and photophysics of triphenylmethane dyes in solid and liquid media. *Chemical reviews* **1993,** *93* (1), 381-433.
29. Donham, L. L.; Gronert, S., Substitution Reactions on Iodine and Bromine: Mechanisms for Facile Halogenations of Heterocycles. *The Journal of organic chemistry* **2019,** *84* (9), 5757-5762.