Supporting Information for

Unsupervised Reaction Pathways Search for the Oxidation of Hypergolic Ionic Liquid - 1-Ethyl-3-Methylimidazolium Cyanoborohydride ($EMIM^+/CBH^-$) as a Case Study

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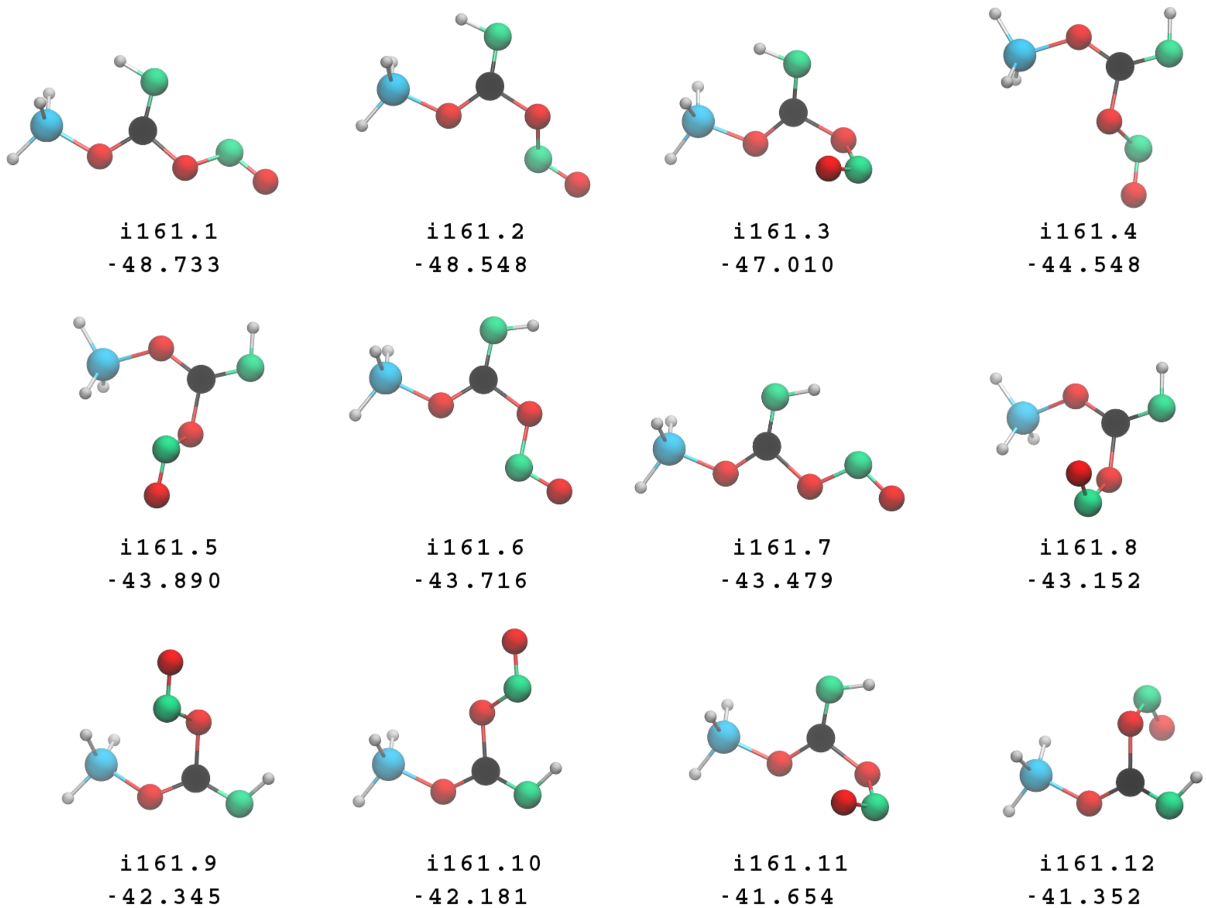

Figure S1. An example of molecules with the same molecular graph and very similar energies. They are represented by one bead in Fig 3 in the manuscript.

The SURGE software can enumerate over all valid Lewis structures of a given input. For example, for C_5H_4, an example input and output would look like:

```
$ ./surge -u C5H4
C5H4  H=4 C=5  nv=5 edges=4-8 DBE=4 maxd=4 maxc=4
>Z generated 19 -> 19 -> 40 in 0.00 sec
```

This generates and, with the -u flag, counts each unique molecule, tabulating there to be 40 in total. These 40 are an exhaustive count and may include exotic-looking isomers (e.g., exceptions to Bredt's rule).

In the above example, the counting is simplified by the fact that all atoms (both the carbons and hydrogens) had fixed valency. In contrast, for the system of interest, multiple atoms of the same element may have differing valencies. For example, for i419 below, two cases exist. First, the nitrogens exist in different valencies: one is tetravalent (formal change +1) and the other is trivalent (formal change 0). Second, the oxygens exist in different valencies: one is monovalent (formal change -1) and the other two are divalent (formal change 0).

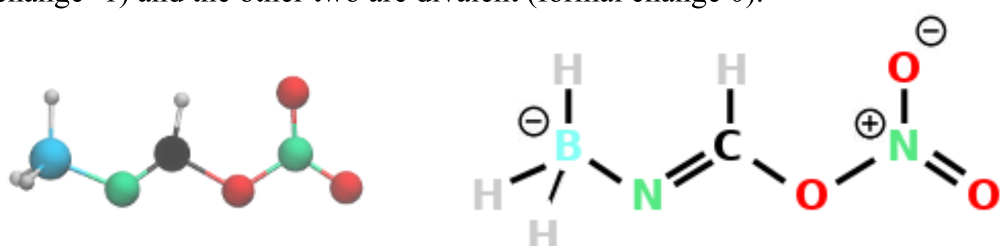

Figure S2 i419 depicted in its lowest-energy configuration (left) and as a Lewis structure (right).

To address this, new pseudo-elements can be created in SURGE to mimic atoms with different valencies. In the above case, i419 would not be generated from inputting in the chemical formula H4BCN2O3, but from the chemical formula H4BCNNpOnO2 where "Np" and "On" are two pseudo-elements with valencies of 4 and 1, respectively, while "N" and "O" are the original elements with their normal valencies of 3 and 2, respectively. For example, an example input and output of this chemical formula should produce:

```
$ ./surge -u -ECn33 -ECt22 -EBn44 -EBx33 -EOn11 -EOp33 -ENp44 BnCNNpO2OnH4
CBnNpNO2OnH4  H=4 C=1 Bn=1 Np=1 N=1 O=2 On=1  nv=7 edges=6-8 DBE=2 maxd=4 maxc=4
>Z generated 94 -> 8886 -> 14229 in 0.00 sec
```

To enumerate over all valid Lewis structures, then, would mean having to first generate all possible chemical formulas with these pseudo-elements before then enumerating over all structure for each formula. Each possible chemical formula must obey chemical intuition and so (1) the formal charges must add to the total charge of the molecule, -1, and (2) the only pseudo-elements (and formal charges) considered are “N” (0), “Np” (+1), “On” (-1), “O” (0), “Op” (+1), “Bx” (0), and “Bn” (-1). This results in 9 possible chemical formulas:

Table S1 Chemical formula possibilities for the system of interest.

Symbol	Bx	Bn	Np	N	Op	O	On
Formal Charge	0	-1	+1	0	+1	0	-1
Formula	Number of Each Pseudo-element						
$BnCNp_2OOn_2H_4$	0	1	2	0	0	1	2
$BnCNNpO_2OnH_4$	0	1	1	1	0	2	1
$BnCNNpOpOn_2H_4$	0	1	1	1	1	0	2
$BnCN_2O_3H_4$	0	1	0	2	0	3	0
$BnCN_2OpOOnH_4$	0	1	0	2	1	1	1
$BxCNp_2On_3H_4$	1	0	2	0	0	0	3
$BxCNNpOOn_2H_4$	1	0	1	1	0	1	2
$BxCN_2O_2OnH_4$	1	0	0	2	0	2	1
$BxCN_2OOn_2H_4$	1	0	0	2	1	0	2

Finally, the last matter is of resonance. Again, SURGE only deals with fixed valencies so resonance structures cannot be considered. While the most common case, a nitro group’s two oxygens, does not matter as they would have the same molecular graph and Lewis structure, more exotic cases can pop up where two resonance structures can have different molecular graphs and thus be double-counted as distinct Lewis structures. To solve this, for each pair of resonance structures, one can be deleted (and for this system of interest, we assume no set of resonance structures spans more than two Lewis structures). Below are the set of chemical substructures that can lead to resonance-pairs and thus are pruned:

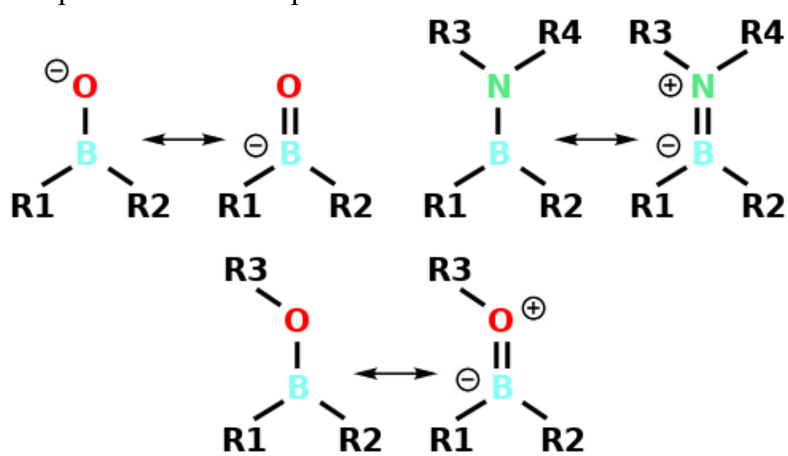

Figure S3 Chemical substructures that lead to redundant resonance-pairs.

After applying this, and removing some Lewis structures deemed exotic (those including an O-O bond), the system of interest can be broken down as follows:

Table S2 Total number of Lewis structures for each chemical formula after removing redundant resonance-pairs.

	Number of Lewis Structures	
Formula	All	No O-O
$BnCNp_2OOn_2H_4$	2755	2233
$BnCNNpO_2OnH_4$	11010	6921
$BnCNNpOpOn_2H_4$	7086	4956
$BnCN_2O_3H_4$	4184	2128
$BnCN_2OpOOnH_4$	13933	7142
$BxCNp_2On_3H_4$	131	131
$BxCNNpOOn_2H_4$	553	393
$BxCN_2O_2OnH_4$	185	85
$BxCN_2OOn_2H_4$	297	194
Total:	40134	24183

Figure S4 Zoom-in picture of Fig 3.a

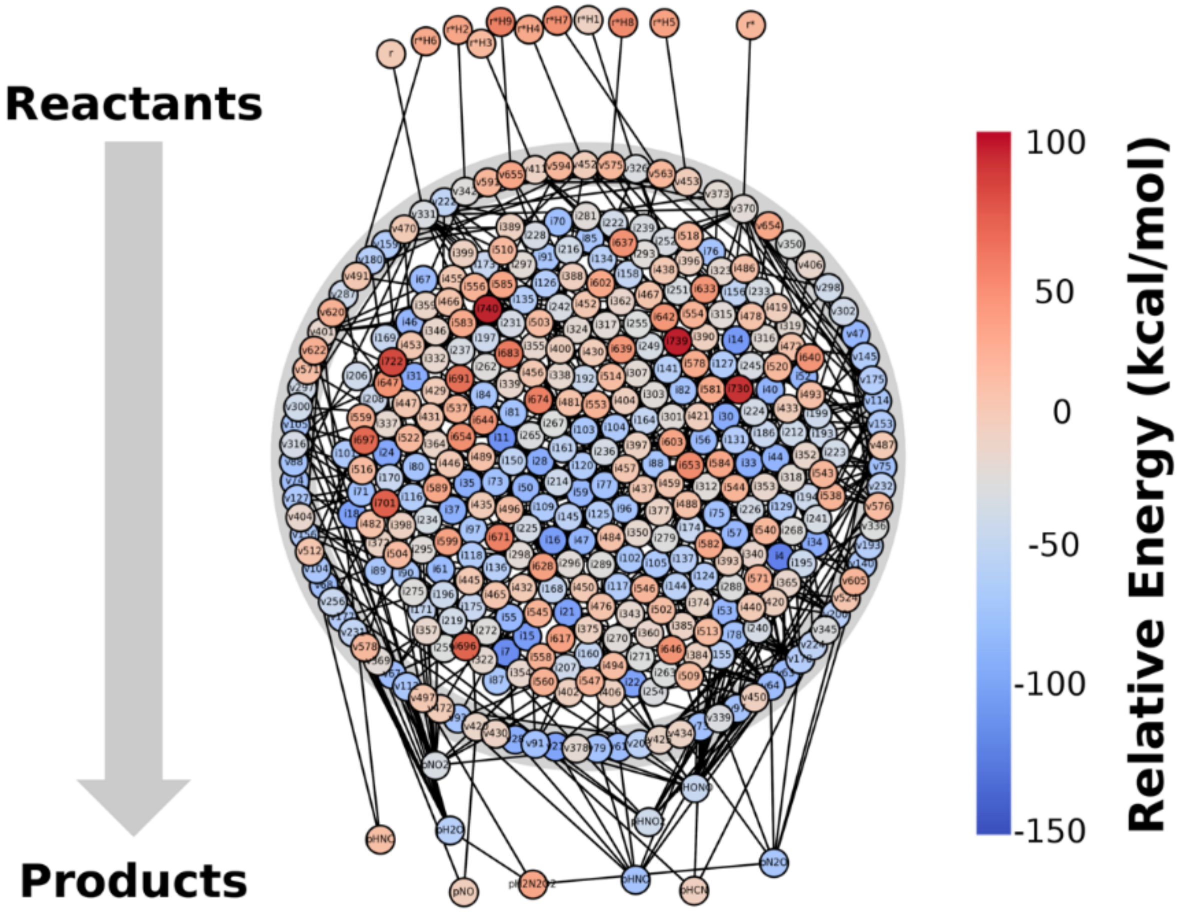

Figure S5 Zoom-in picture of Fig 3.b

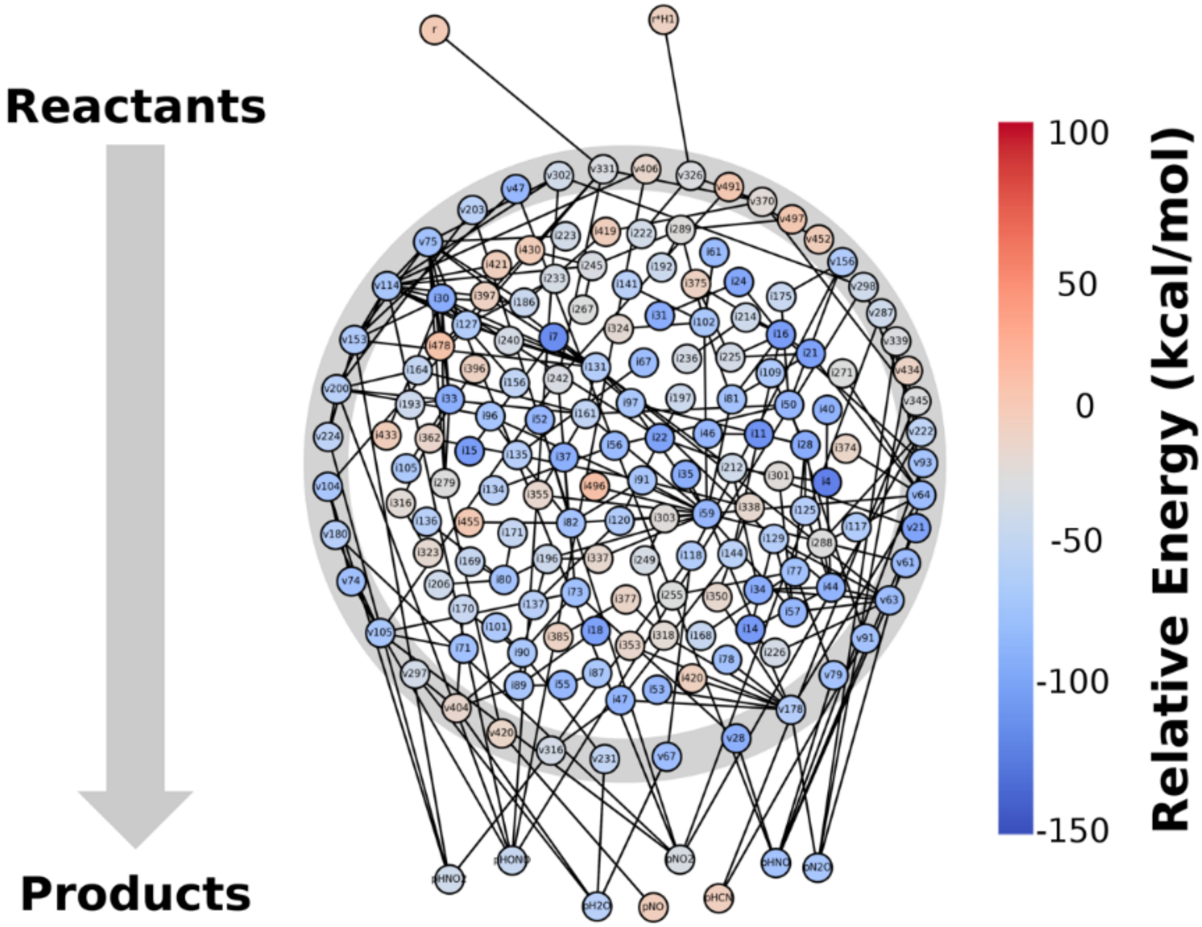

Figure S6 Zoom-in picture of Fig 3.c