

Accessory Publication

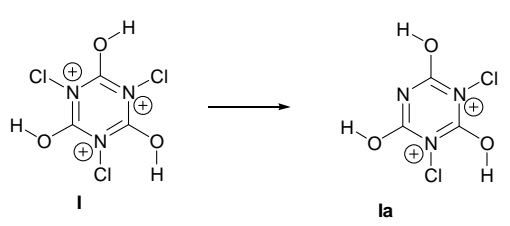
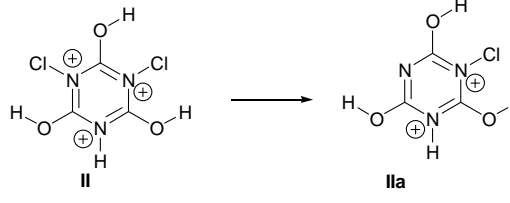
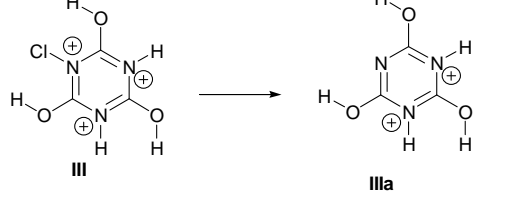
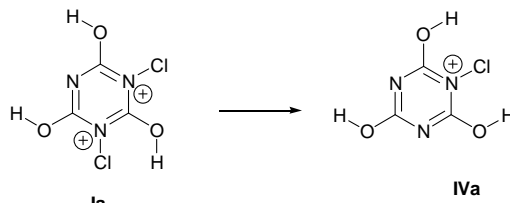
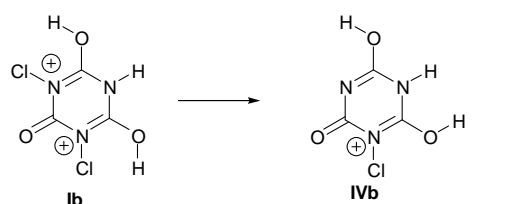
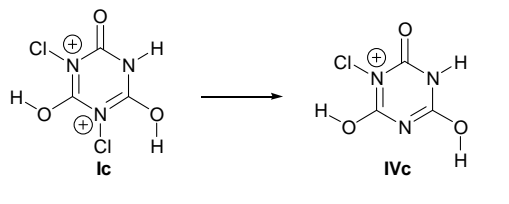
Chlorination of Aromatics with Trichloroisocyanuric Acid (TCICA) in Brønsted Acidic Imidazolium Ionic Liquid [BMIM(SO₃H)][OTf]; An Economical, Green, Protocol for the Synthesis of Chloroarenes.[§]

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Table S1. B3LYP/6-31+G(d,p) Reaction Enthalpies and Gibbs Free Energies (kcal/mol) for Cl^+ Generation from Protonated TCICA at 25 °C and 50 °C under 1 atm.

| Reaction | ΔG (25 °C) | ΔH (25 °C) | ΔH (50 °C) |
|---|--------------------|--------------------|--------------------|
|  | -48.3 | -39.2 | -39.3 |
|  | -51.0 | -42.6 | -42.8 |
|  | -52.5 | -44.1 | -44.2 |
|  | 61.4 | 69.9 | 69.8 |
|  | 65.3 | 74.1 | 74.0 |
|  | 48.9 | 57.2 | 57.0 |

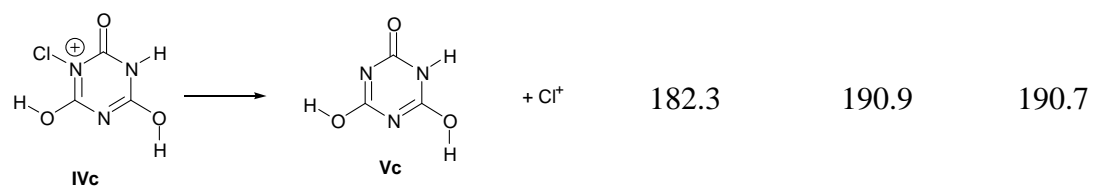
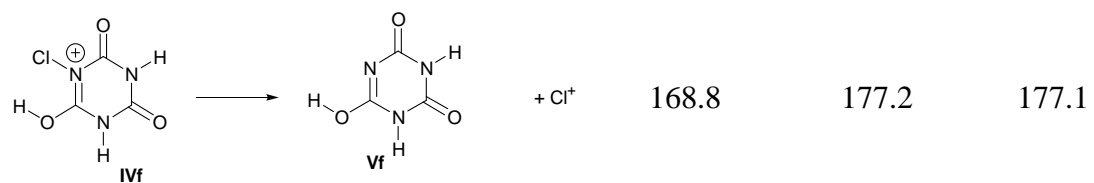
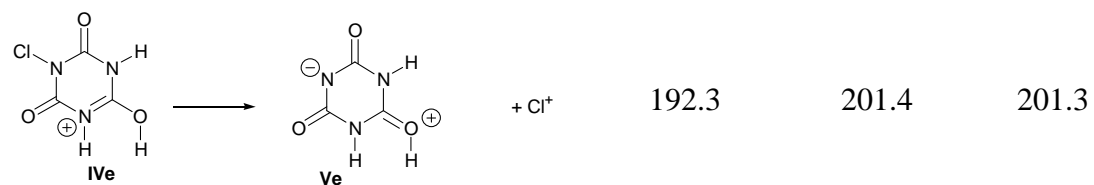
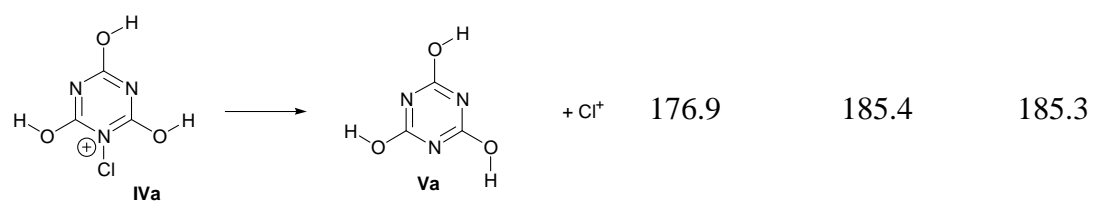
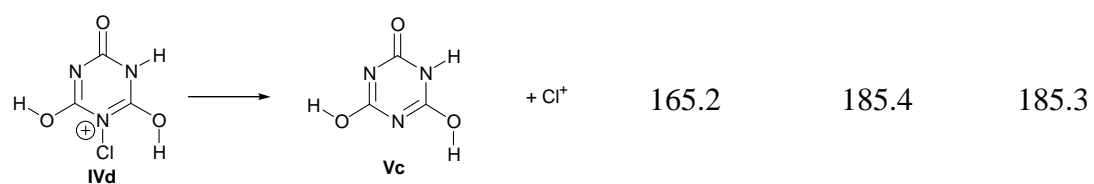
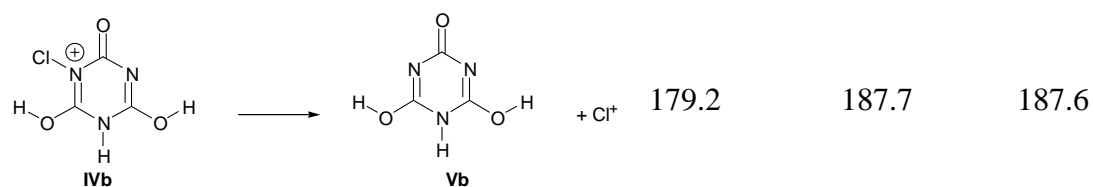
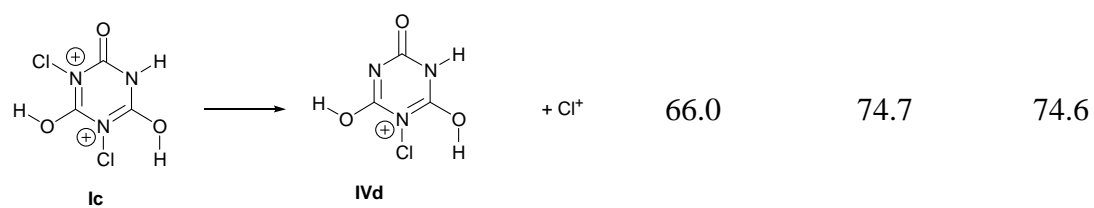


Table S2. B3LYP/6-31+G(d,p) Relative Enthalpies and Gibbs Free Energies (kcal/mol) for Protonated Dications from Dichlorinated Compounds at 25 °C and 50 °C under 1 atm.

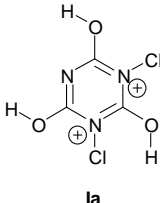
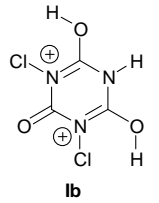
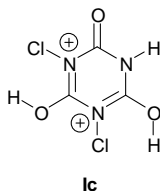
| |  |  |  |
|--------------------|---|---|--|
| | Ia | Ib | Ic |
| ΔG (25 °C) | (0) | 2.1 | 5.8 |
| ΔH (25 °C) | (0) | 2.6 | 6.4 |
| ΔH (50 °C) | (0) | 2.6 | 6.4 |

Table S3. B3LYP/6-31+G(d,p) Relative Enthalpies and Gibbs Free Energies (kcal/mol) for Protonated Cations from Monochlorinated Compounds at 25 °C and 50 °C under 1 atm.

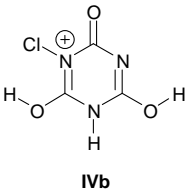
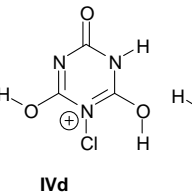
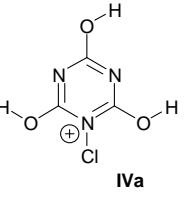
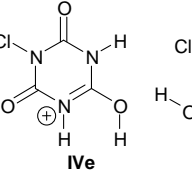
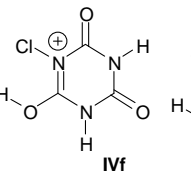
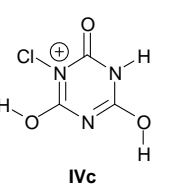
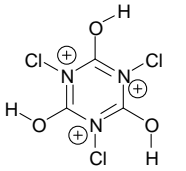
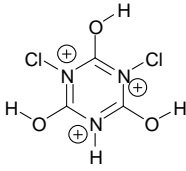
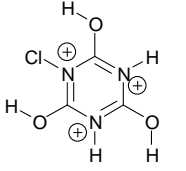
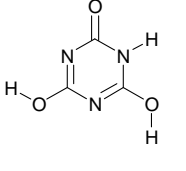
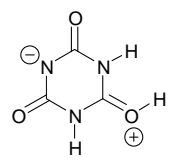
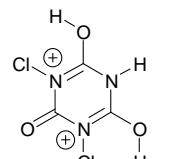
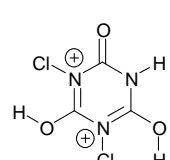
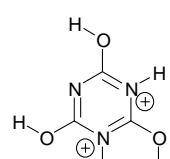
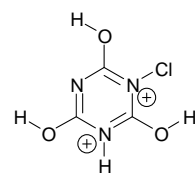
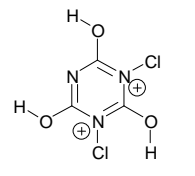
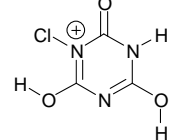
| |  |  |  |  |  |  |
|--------------------|---|---|---|--|---|---|
| | IVb | IVd | IVa | IVe | IVf | IVc |
| ΔG (25 °C) | 12.7 | 17.1 | 6.7 | 5.5 | 2.8 | (0) |
| ΔH (25 °C) | 13.2 | 17.5 | 6.4 | 6.1 | 2.6 | (0) |
| ΔH (50 °C) | 13.2 | 17.5 | 6.4 | 6.1 | 2.6 | (0) |

Table S4. Energy of Various Cationic Species Calculated by B3LYP/6-31+G(d,p)

| Compound | Symmetry | E, hartree | ZPE, hartree | G, hartree at 25 °C ^a | H, hartree at 25 °C ^a | H, hartree at 50 °C ^a |
|---|-----------------|---------------|--------------|-------------------------------------|-------------------------------------|-------------------------------------|
| Cl ⁺ | O _h | -459.5798013 | 0.000000 | -459.594824 | -459.577441 | -459.577441 |
|  | C _{3h} | -1885.2022611 | 0.083167 | -1885.156258 | -1885.106804 | -1885.105028 |
|  | C _s | -1425.6675741 | 0.093583 | -1425.610132 | -1425.563001 | -1425.561376 |
|  | C _s | -966.1325355 | 0.104123 | -966.062406 | -966.018736 | -966.017264 |
|  | C ₁ | -506.1193939 | 0.080003 | -506.070952 | -506.031558 | -506.030402 |

| | | | | | | |
|---|----------------|--------------|----------|-------------|-------------|-------------|
|  | C ₁ | -506.1029178 | 0.079236 | -506.055643 | -506.015586 | -506.014403 |
|  | C ₁ | -506.1181607 | 0.080483 | -506.068941 | -506.030017 | -506.028875 |
|  | C ₁ | -965.9944462 | 0.082369 | -965.945696 | -965.902949 | -965.901607 |
|  | C ₁ | -965.9945159 | 0.081427 | -965.947482 | -965.903412 | -965.902029 |
|  | C ₁ | -965.9990941 | 0.081556 | -965.951835 | -965.907976 | -965.906604 |
|  | C ₁ | -506.1360978 | 0.079948 | -506.087995 | -506.048163 | -506.046999 |

| | | | | | | |
|---|----------------|---------------|----------|--------------|--------------|--------------|
|  | C _s | -506.0910666 | 0.077499 | -506.046138 | -506.004971 | -506.003740 |
|  | C ₁ | -1425.6814552 | 0.082836 | -1425.634934 | -1425.587687 | -1425.586115 |
|  | C ₁ | -1425.6753327 | 0.082666 | -1425.629028 | -1425.581709 | -1425.580137 |
|  | C ₁ | -965.982783 | 0.080988 | -965.936039 | -965.892203 | -965.890815 |
|  | C ₁ | -965.975796 | 0.081022 | -965.929095 | -965.885229 | -965.883851 |
|  | C ₁ | -506.6241355 | 0.104503 | -506.551239 | -506.511512 | -506.510261 |

| | | | | | | |
|---|-------|---------------|----------|--------------|--------------|--------------|
|  | C_1 | -966.1567095 | 0.093878 | -966.096596 | -966.053473 | -966.052074 |
|  | C_1 | -1425.6857796 | 0.083307 | -1425.638337 | -1425.591839 | -1425.590290 |
|  | C_s | -966.0047207 | 0.082275 | -965.956299 | -965.913171 | -965.911822 |

^a under 1 atm.