Reactions of benzene

Iðunn Björg Arnaldsdóttir

September 2025

A. Dehydrogenation of Cyclohexane to Form Benzene

Q1: Write balanced chemical equations for each of the three dehydrogenation steps in your report. What other products are involved?

$$\begin{aligned}
\text{Step 1:}\quad & C_6H_{12} \longrightarrow C_6H_{10} + H_2 \\
\text{Step 2:}\quad & C_6H_{10} \longrightarrow C_6H_8 + H_2 \\
\text{Step 3:}\quad & C_6H_8 \longrightarrow C_6H_6 + H_2 \\
\text{Overall:}\quad & C_6H_{12} \longrightarrow C_6H_6 + 3\,H_2
\end{aligned} \tag{1}$$

✓

Q2: Write the calculated ground state energy of each molecule in your report.

Using Hartree-Fock with the 3-21G basis set, the ground state energies of the molecules involved in the dehydrogenation of cyclohexane were calculated as:

$$\begin{aligned}
E_{C_6H_{12}} &= -232.91690 \text{ Ha} \\
E_{C_6H_{10}} &= -231.72915 \text{ Ha} \\
E_{C_6H_8} &= -230.54323 \text{ Ha} \\
E_{C_6H_6} &= -229.41945 \text{ Ha} \\
E_{H_2} &= -1.12296 \text{ Ha}
\end{aligned}$$

✓

Q3: Calculate the reaction energy for each of the three steps in the dehydrogenation of cyclohexane. Draw an energy diagram showing the three steps of the reaction.

The reaction energy for each step can be calculated using the formula:

$$\Delta E_{\text{reaction}} = \sum E_{\text{products}} - \sum E_{\text{reactants}} \tag{2}$$

Table 1: *Reaction energies, calculated using equation 3, for each step in the dehydrogenation of cyclohexane (see reaction 1). The 3-21G basis set was used for the Hartree-Fock calculations.*

Reaction Step	Energy [Ha]	Energy [eV]
Step 1	0.06479	1.763
Step 2	0.06296	1.713
Step 3	0.00083	0.022

✓

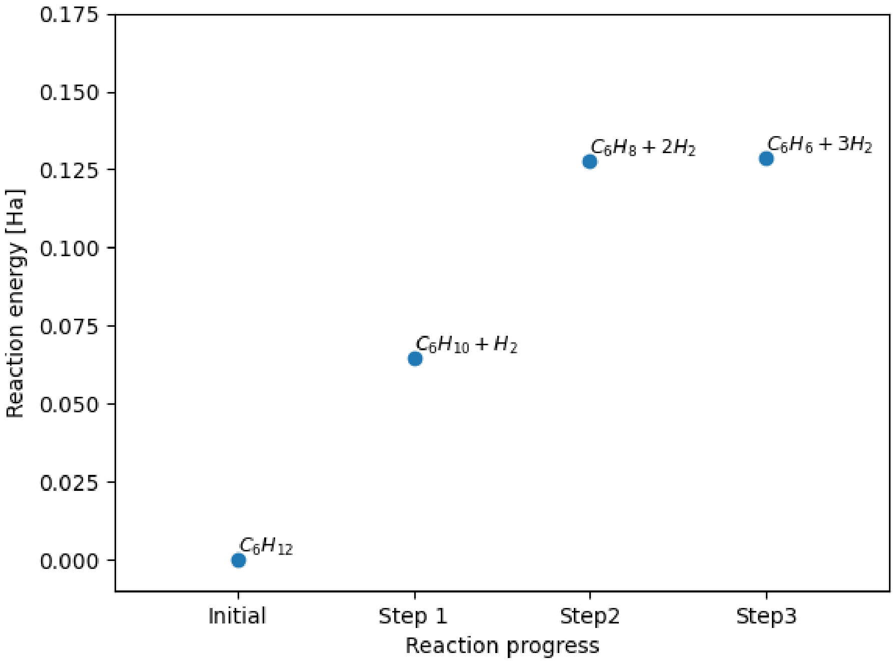


Figure 1: *Accumulative reaction energy for the dehydrogenation of cyclohexane relative to the initial energy of cyclohexane using the 3-21G basis set.*

Q4: Make a table of the reaction energy in the three steps of the dehydrogenation and compare the results obtained from the two basis sets.

Using Hartree-Fock with the 6-31G basis set, the ground state energies of the molecules involved in the dehydrogenation of cyclohexane were calculated as:

$$E_{C_6H_{12}} = -234.11102 \text{ Ha}$$
$$E_{C_6H_{10}} = -232.92686 \text{ Ha}$$
$$E_{C_6H_8} = -231.74402 \text{ Ha}$$
$$E_{C_6H_6} = -230.62447 \text{ Ha}$$
$$E_{H_2} = -1.12683 \text{ Ha}$$

✓

Comparison between calculated reaction energies for the 3-21G and the 6-31G basis s
be found in table 2.

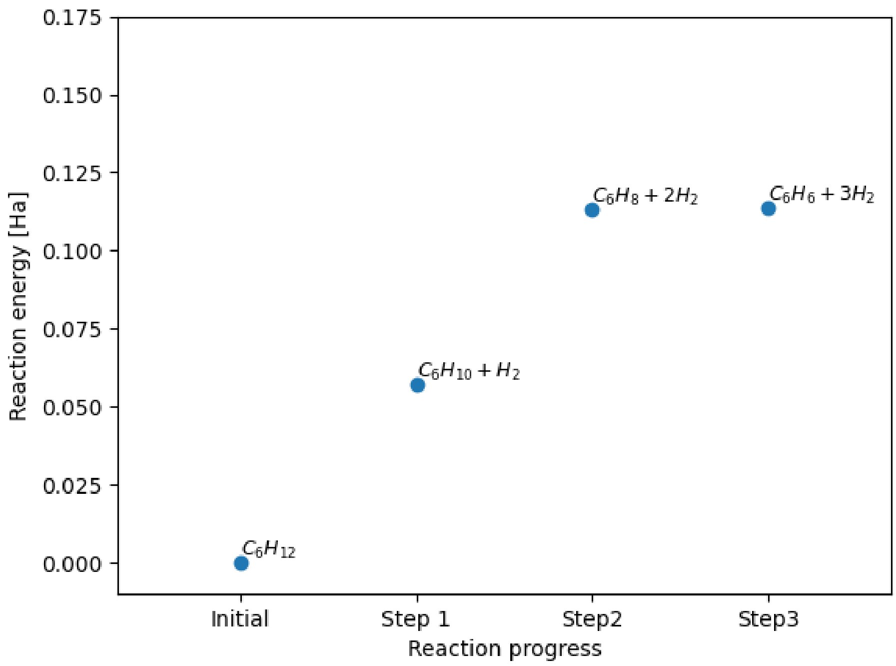
Table 2: *Comparison of reaction energies for dehydrogenation of cyclohexane, ca equation 3, using the 3-21G and the 6-31G basis sets.*

Reaction Step	E_{3-21G} [Ha]	E_{6-31G} [Ha]
Step 1	0.06479	0.05733
Step 2	0.06296	0.05602
Step 3	0.00083	-0.00729

✓

note the change in sign when basis set is increased

Q5: Draw an energy diagram based on the numbers obtained using the larger basis set.



✓

Figure 2: *Accumulative reaction energy for the dehydrogenation of cyclohexane relative to the initial energy of cyclohexane using the 6-31G basis set.*

Q6: Are the reaction steps exothermic or endothermic? What is the energy change during hydrogenation of benzene? How well do the calculated results agree with experimental observations?

For the 3-21G basis set, all reaction steps were calculated to be endothermic, i.e., they had positive energy changes. However, for the last step (step 3 in reaction 1), the reaction energy was calculated to be negative using the 6-31G basis set, predicting this step to be exothermic. The total reaction energy was predicted to be endothermic for both basis sets:

$$E_{\text{total, 3-21G}} = E_1 + E_2 + E_3 = 0.12858 \text{ Ha}, \quad E_{\text{total, 6-31G}} = E_1 + E_2 + E_3 = 0.10606 \text{ Ha}.$$

✓

The experimental reaction enthalpy for the dehydrogenation of cyclohexane is $\Delta_r H^\circ = 0.0782 \pm 0.0002$ Ha [1]. Thus, the 3-21G basis set overestimates the energy change by 0.0503 Ha, corresponding to a relative error of 64.42%. The 6-31G basis set, however, is only 0.0279 Ha away from the experimental value, giving a relative error of 35.63%.

B. Reaction of nitronium cation with benzene

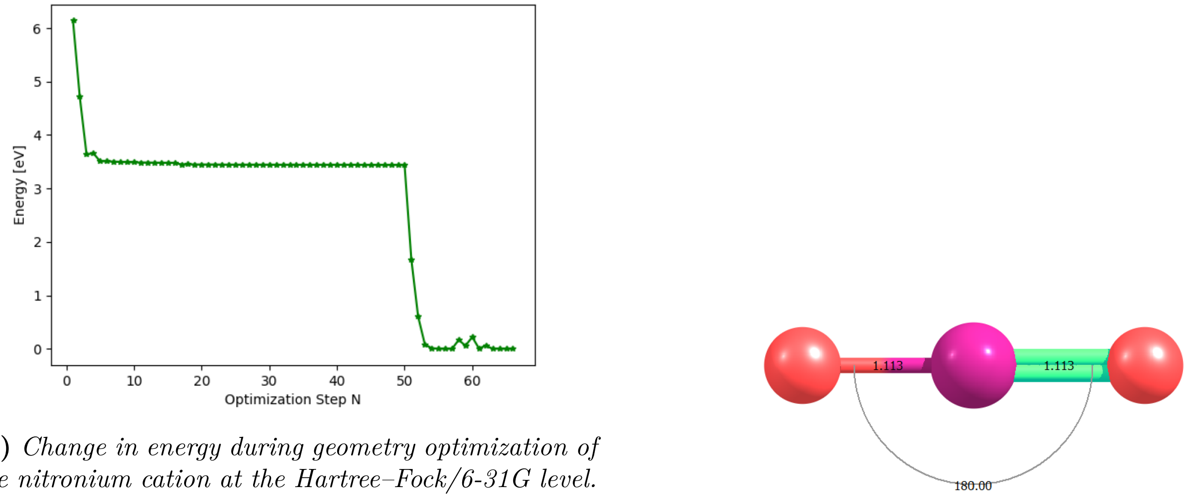
Q7: What is the ground state energy of the nitronium cation? Is the molecule bent or linear? Are the N-O bond lengths identical or different?

The ground-state energy of the nitronium cation was calculated at the Hartree–Fock level with the 6-31G basis set to be

$$E_{NO_2^+} = -203.51102 \ Ha = -5537.8190 \ eV.$$

✓

The optimized geometry is linear, with two equivalent N–O bond lengths. This equivalence reflects the delocalized bonding (resonance) in the cation (see Fig. 3b).



✓

(a) *Change in energy during geometry optimization of the nitronium cation at the Hartree–Fock/6-31G level. The energy is plotted relative to the optimized value, i.e.* $E = (E_{\text{calc}} - E_0)\cdot\frac{27.2116\ eV}{1\ Ha}$*, with* $E_0 = -203.51102$ *Ha.*

(b) *Ground-state geometry of the nitronium cation.*

Figure 3: *Optimized structure and convergence behavior of the nitronium cation.*

Q8: Where is the positive charge mostly located? Based on your calculation, draw the Lewis dot structure that best represents the nitronium cation.

The positive charge in the nitronium cation is primarily localized on the nitrogen atom, while the electron density is symmetrically distributed mostly over the two oxygen atoms (Fig. 4a). Consequently, the Lewis structure that best represents the nitronium cation places the positive charge on nitrogen, which forms two equivalent N=O double bonds (Fig. 4b).

✓

(a) *Electron density distribution of the nitronium cation. Blue indicates regions of low electron density, while red indicates regions of high electron density.*

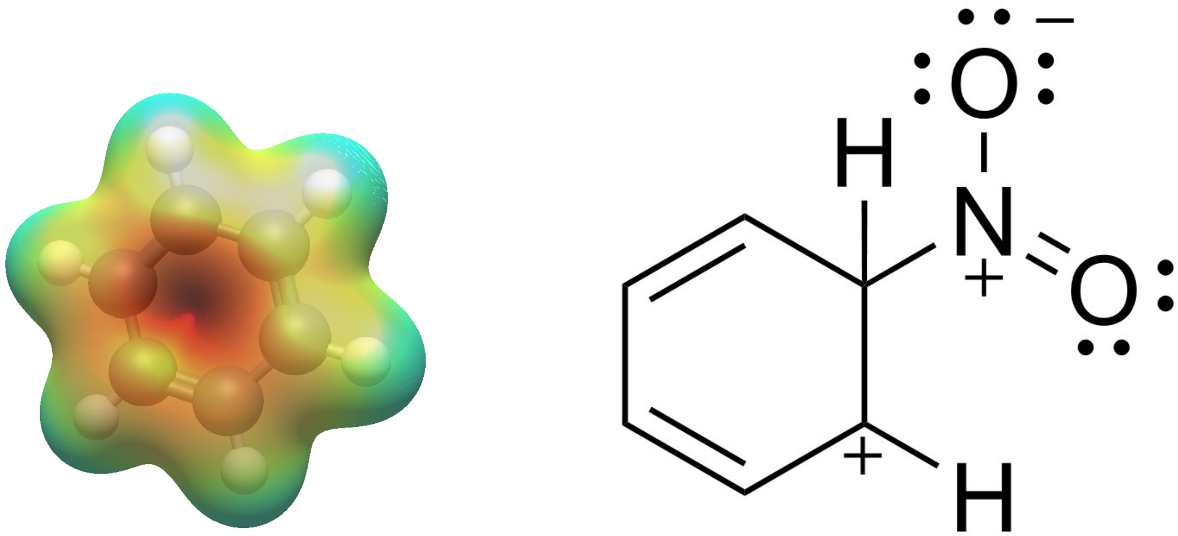
(b) *Lewis structure that best represents the ground state of the nitronium cation, consistent with the calculated electron density.*

Figure 4: *Electron density of the nitronium cation calculated using Hartree-Fock with the 6-31G basis set.*

Q9: Judging from the electrostatics, how do you expect the nitronium ion to react with the benzene molecule (which part of the nitronium ion will most likely collide with the benzene molecule and in what region?). Draw a Lewis structure of the nitronium/benzene adduct.

The benzene molecule has high electron density on the carbon atoms (see Fig. 5a), while the nitronium cation has a positive charge which is mostly located on the nitrogen atom (see Fig. 4a). Thus, the electron cloud on the benzene ring is attracted to the positive charge on the nitrogen atom and one of the carbon atoms connects to the nitrogen through a nucleophilic attack, forming an intermediate-adduct (see Fig. 5b and Fig. 8).

✓



✓

(a) *Calculated electron density for the benzene molecule at the HF/6-31G level.*

(b) *Lewis structure of the intermediate nitronium/benzene adduct of the electrophilic substitution reaction to form nitrobenzene.*

Figure 5

Q10: Place a picture of the optimized structure in your report. How do you describe the bonding (get the C–C bond lengths in the ring)?

The optimized structure of the benzene–nitronium adduct (Fig. 6) shows that the C–C bond lengths in the aromatic ring are no longer equal, in contrast to benzene. Nevertheless, partial resonance should remain between the ortho-meta and meta-para positions, see Fig. 8.

✓

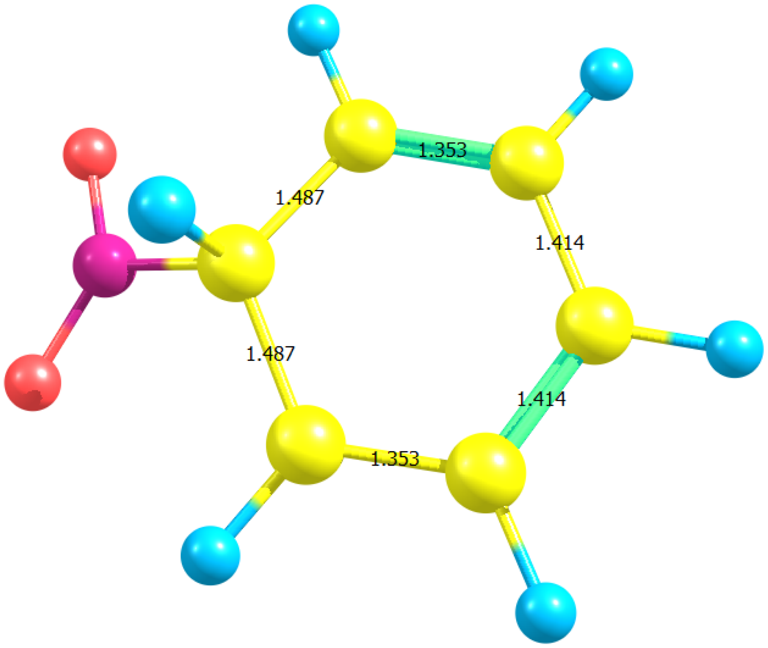


Figure 6: *Optimized geometry of the benzene–nitronium adduct. The benzene ring no longer exhibits full resonance, as evidenced by the unequal C–C bond lengths. Partial delocalization should theoretically remain between the ortho-meta and meta-para positions (see Fig. 8), but it is not evident in the optimized structure.*

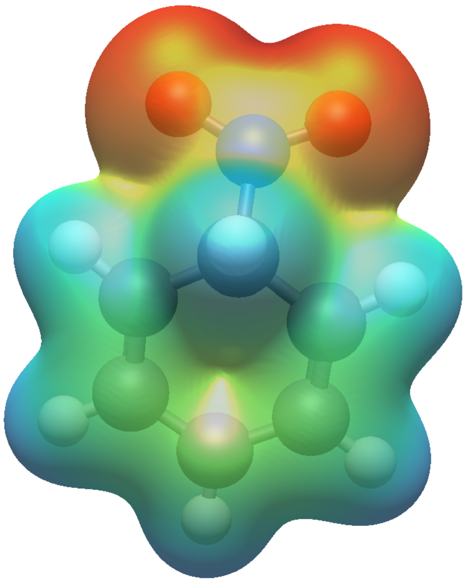
Q11: What is the binding energy of the adduct (energy of the adduct minus the energy of reactants, i.e. isolated nitronium ion and benzene molecule).

Binding energy of a giving molecule is given by the following equation

$$E_{\text{Binding}} = \sum E_{\text{Products}} - \sum E_{\text{Reactants}}. \tag{3}$$

The calculated energy of each molecule involved in the reaction, using HF/6-31G, was $E_{NO_2^+} = -203.51102\ Ha$, $E_{C_6H_6} = -230.62447\ Ha$ and $E_{adduct} = -434.23437\ Ha$. Thus, $E_{Binding-adduct} = -0.09888\ Ha = -2.691\ eV$. ✓

Q12: Show a picture of the electrostatic potential map of the adduct in your report.

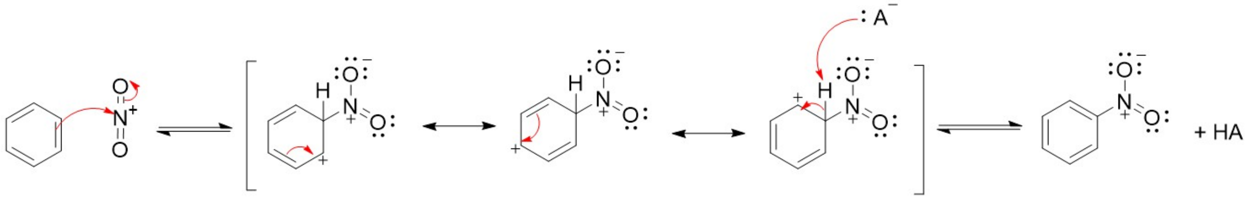


✓

Figure 7: *Calculated electron density for the optimized geometry of the benzene-nitronium adduct.*

Q13: Which proton would you expect is easiest to remove? Why?

The nitronium group is electron withdrawing since it connects through the nitrogen atom which has partially a positive charge. This means that the nitronium groups drags towards itself the electron density of nearby atoms; which means the hydrogen connected to the same carbon as the nitronium group becoms more loosely bound and it becoms easier to remove than other hydrogen atoms, see Fig. 8.



✓

Figure 8: *Reaction mechanism for the electrophilic substitution between benzene and a nitronium cation to form nitrobenzene.*

Q14: Is it necessary to carry out a calculation for the single proton to determine its energy? Is the total energy of your product and the proton higher or lower than that of the charged adduct?

It is not necessary (nor meaningful) to perform an SCF calculation on an isolated proton. The SCF algorithm is based upon the electronic hamiltonian and nuclear energies are only included through nuclear repulsion between multiple atoms. Since a proton has no electrons and only one nucleus, the calculation will return no value or zero. We would need to include the energy of the base used and its protonated form to estimate the energy of the removed proton. ✓

The calculated energy of the nitrobenzene was $E_{nitrobenzene} = -433.97766\ Ha$ so the energy of the proton and nitrobenzene is higher than the energy of the charged adduct. In total the reaction energy to form nitrobenzene from benzene and nitronium is $E_{Binding} = E_{nitrobenzene} - E_{NO_2^+} - E_{C_6H_6} = 0.15784\ Ha = 4.2950\ eV$. Since the binding energy is positive the nitrobenzene is thermodynamically less stable than the initil reactants. ✓

Q15: Can you name another (quite well known) aromatic compound containing nitro groups that is even more unstable thermodynamically?

One example of an thermodynamically unstable aromatic compound containing nitro groups is the explosive 2,4,6-trinitrotoluene (otherwise known as TNT). It is even less stable than nitrobenzene since multiple nitro groups withdraw electron density strongly (reduce aromatic stabilization), and thus decrease even more the thermodynamic stability. ✓

References

[1] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, “Heats of organic reactions. iv. hydrogenation of some dienes and of benzene”, Journal of the American Chemical Society **58**, 146–153 (1936).