Products and Mechanisms of the Reactions of 1,3-Butadiene with Chlorine Atoms In Air

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Introduction

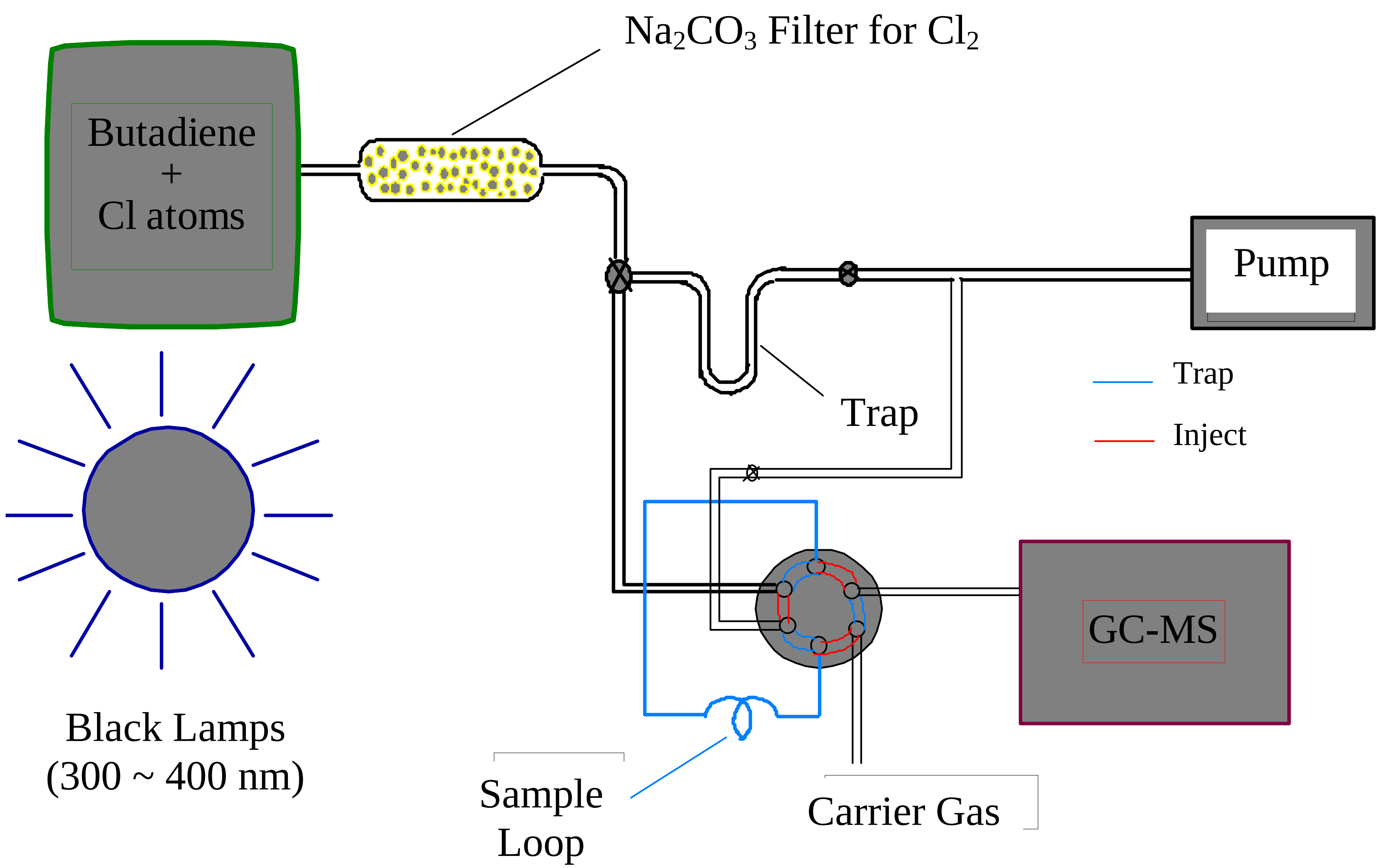
- Cl atoms may be generated by reactions of sea salt particles transported inland with air masses.

- A potential approach to investigate the importance of chlorine atom chemistry in the coastal areas is to identify the products and mechanisms of its reactions with organics, e.g. 1,3-butadiene.

- 1,3-Butadiene is an EPA designated Hazardous Air Pollutant (HAP). One of its major sources is automobile emissions.

- Both 1,3-butadiene and chlorine atoms can be abundant in coastal areas.

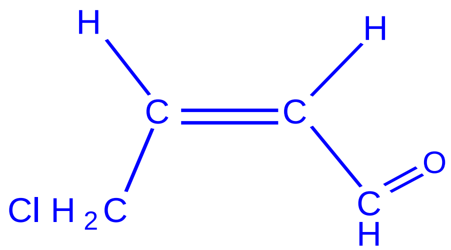
GC-MS Experimental Apparatus



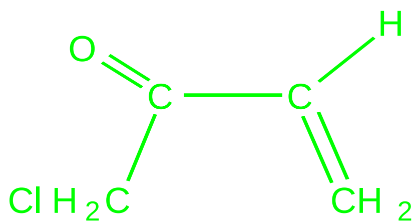
Goals

- Elucidate the mechanisms of the reaction of Cl atoms with 1,3-butadiene with or without NO

- Identify unique chlorine-containing products, which could serve as markers for Cl chemistry in coastal areas, from the Cl-butadiene reaction
e.g. :

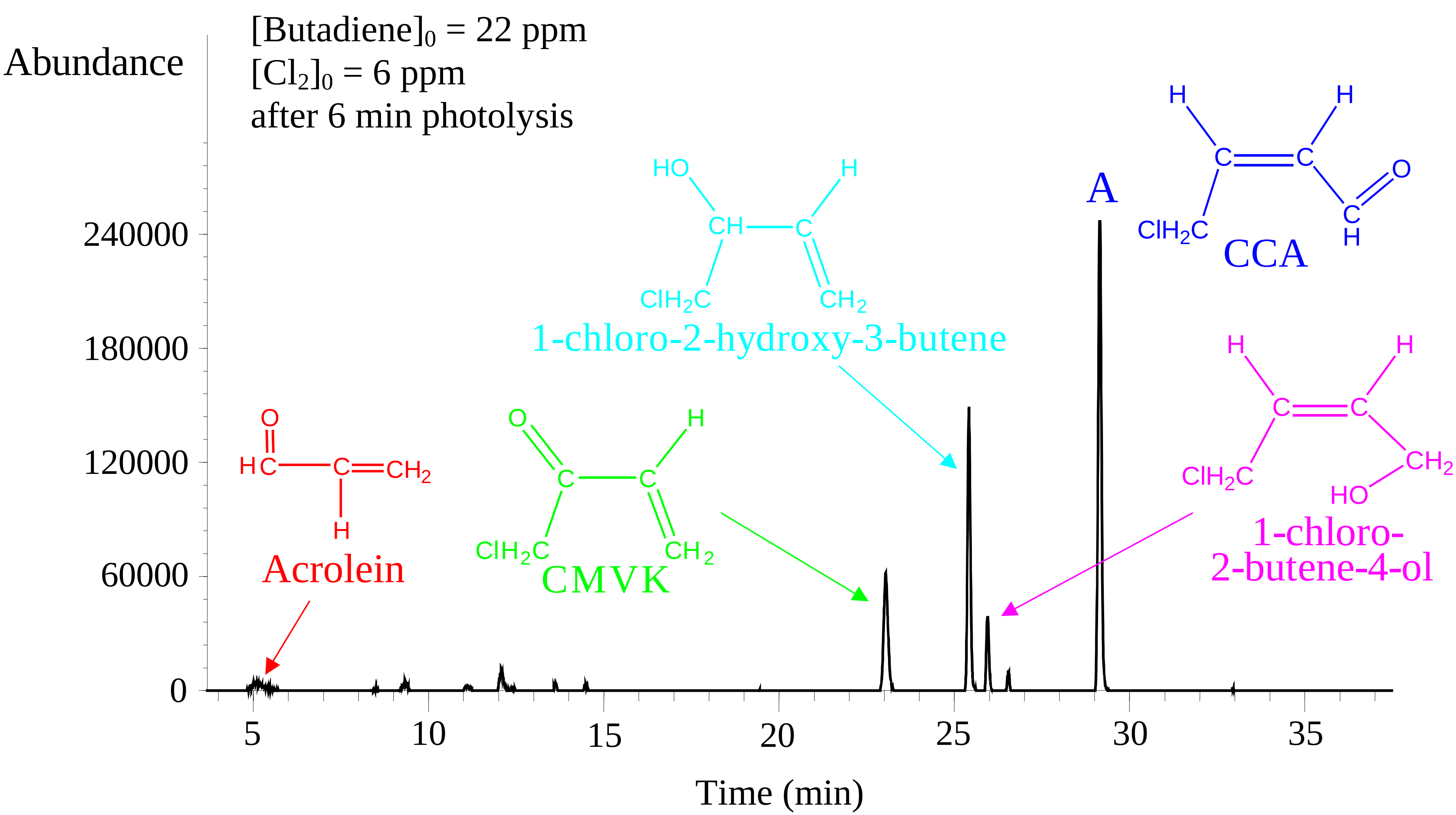


4-chlorocrotonaldehyde (CCA)



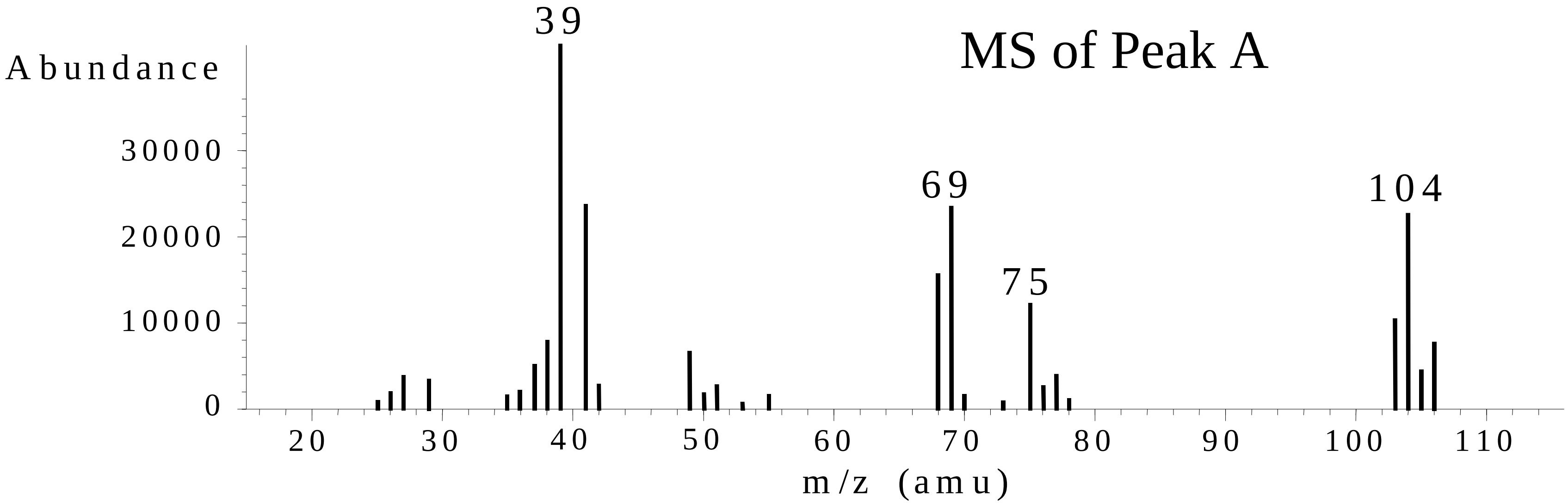
chloromethyl vinyl ketone (CMVK)

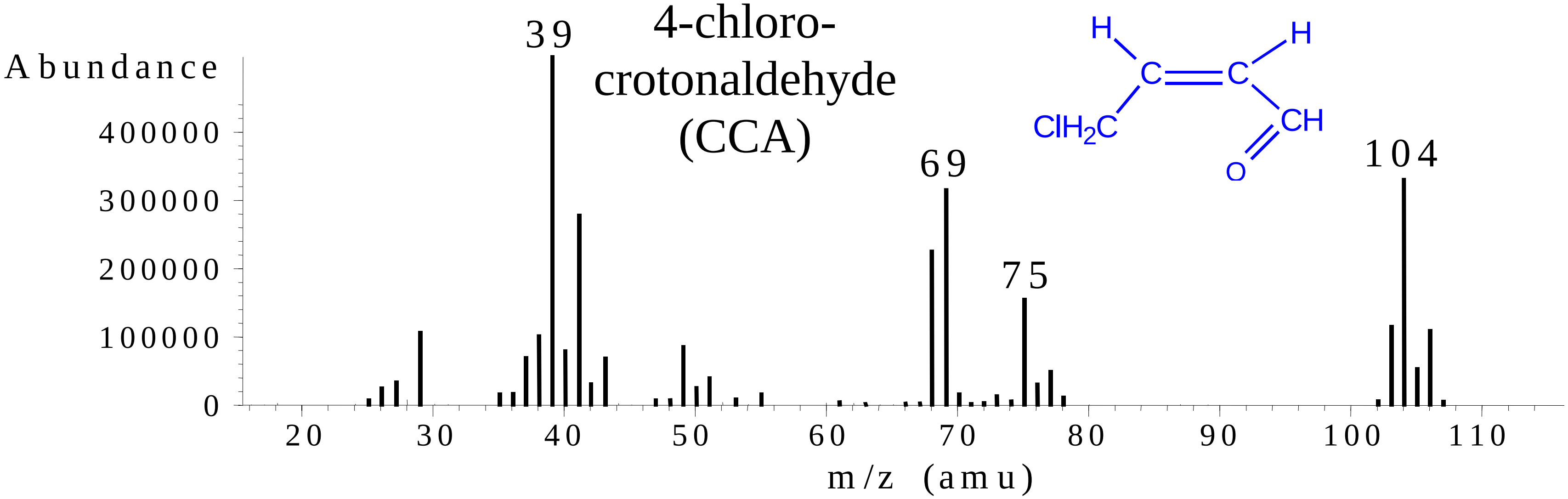
Gas Chromatogram of Products of 1,3-Butadiene + Cl



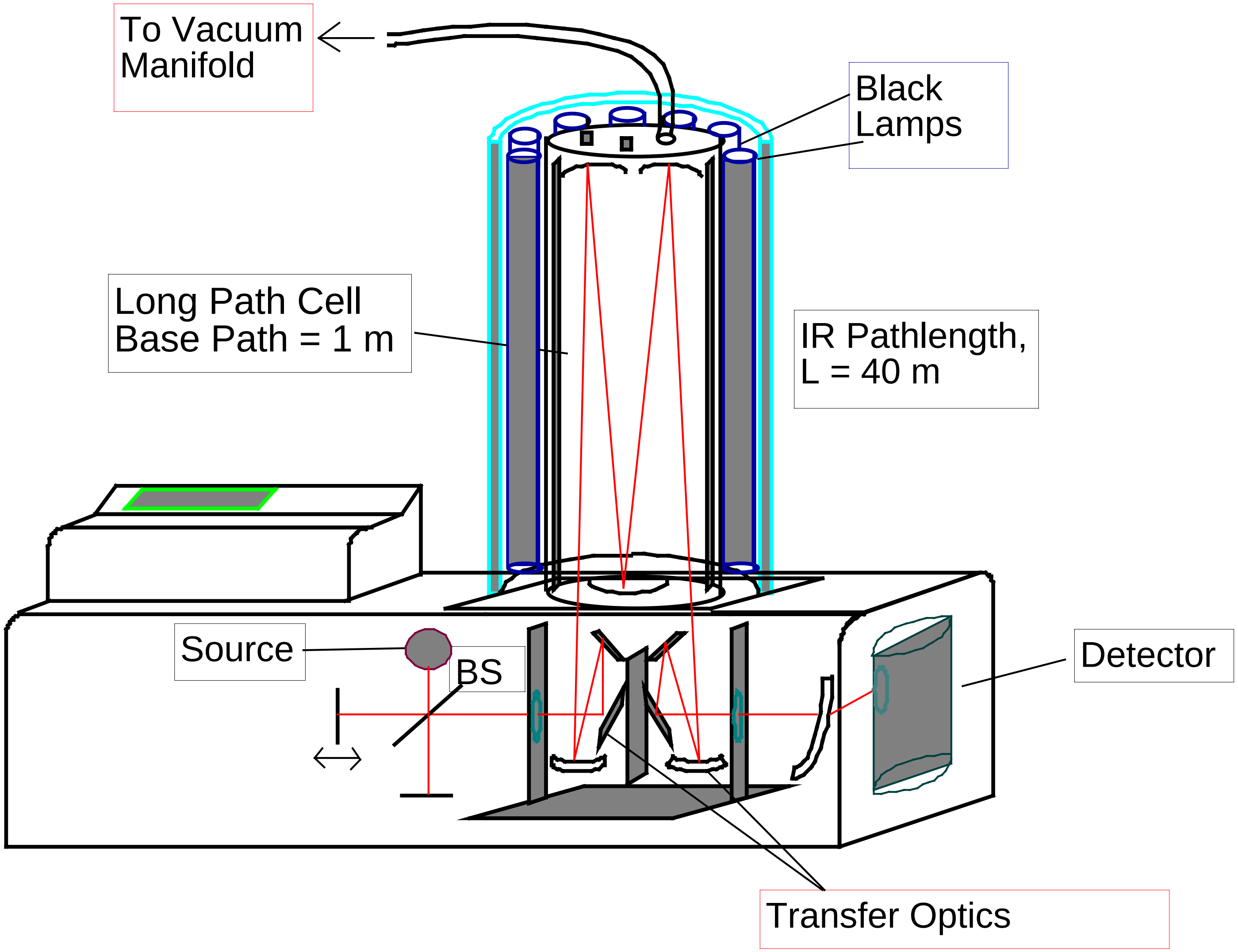
- Products were identified by comparison with the retention times and mass patterns of the authentic compounds.

One Example of Peak Identification: Mass Spectra of Peak A and CCA Reference

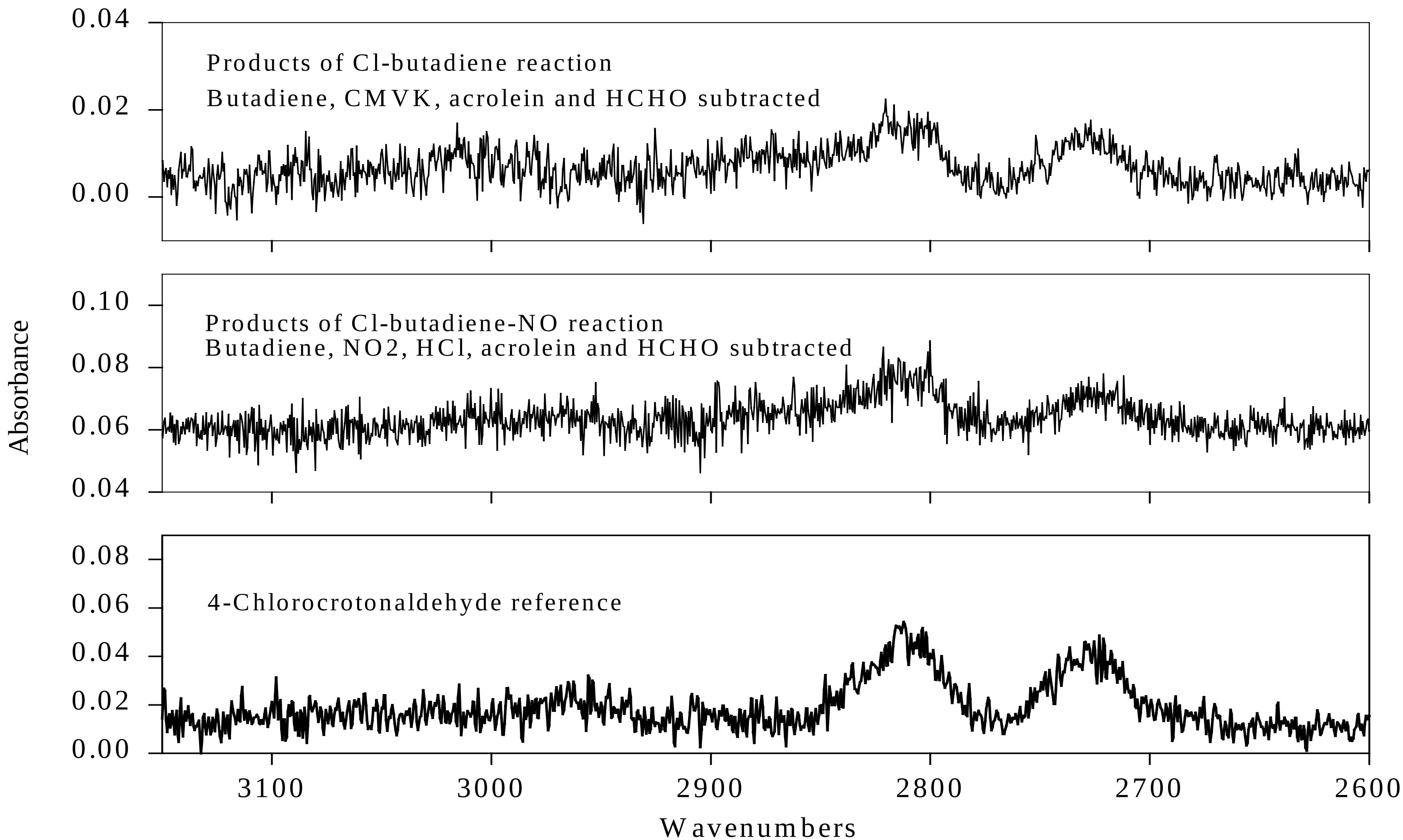




FTIR Experimental Apparatus

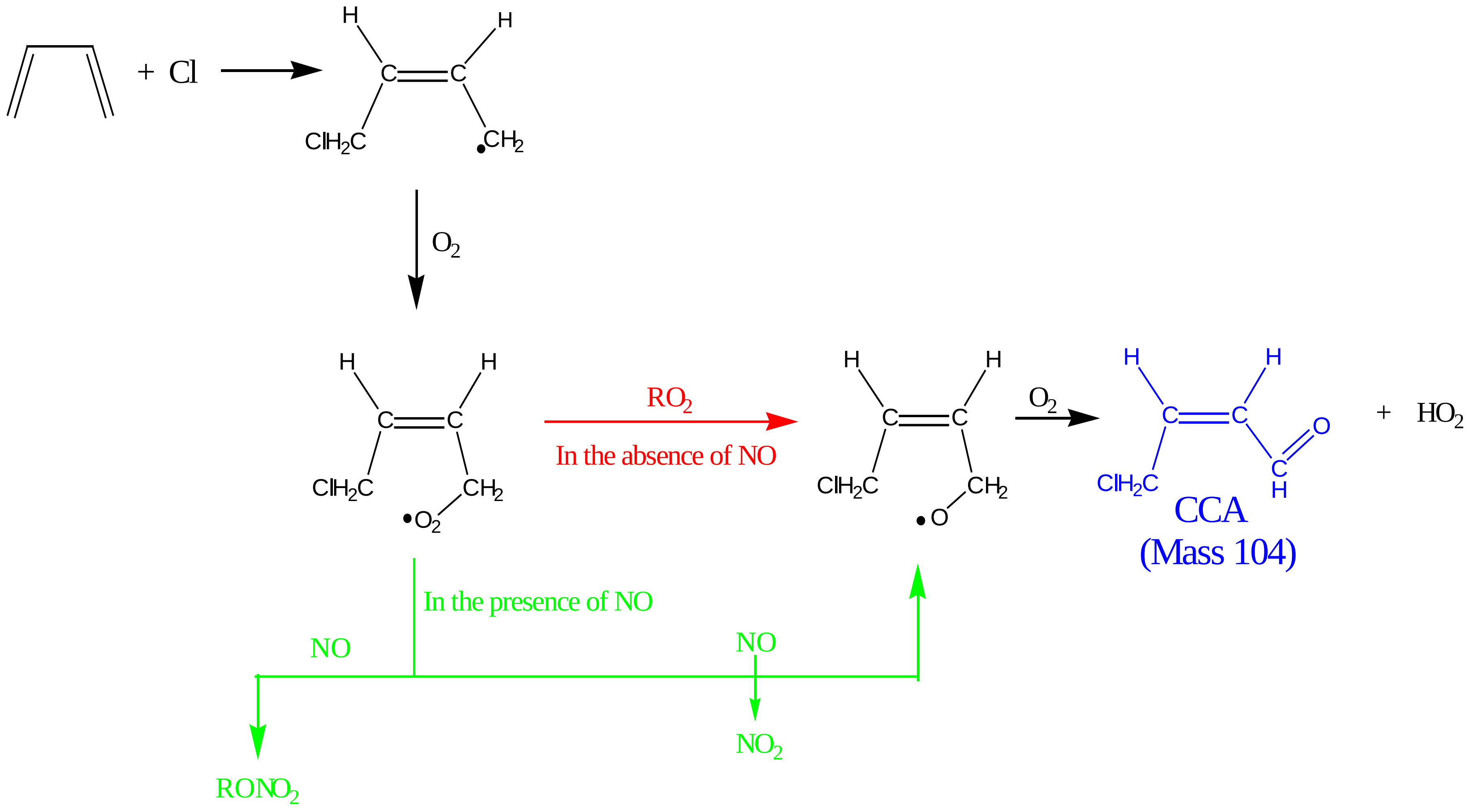


FTIR Spectra of the Cl-Butadiene Reaction and CCA Reference



- 4-Chlorocrotonaldehyde was identified as a product of the Cl-butadiene reaction in the presence and absence of NO.

Partial Reaction Scheme for the Cl-Butadiene Reaction —— CCA Formation



Product Yields

Products	w/ NO (± 2σ)	w/o NO (± 2σ)
CCA	35 ± 7 %	35 ± 3 %
CMVK	< 9 %	18 ± 3 %
Acrolein	44 ± 7 %	6 ± 4 %
HCHO	52 ± 7 %	7 ± 1 %
CO	11 ± 4 %	—
HCl	12 ± 6 %	—
NO_2	√	—
organic nitrate	√	—
1-chloro-2-hydroxy-3-butene	—	√
1-chloro-2-butene-4-ol	—	√

$[1,3\text{-Butadiene}]_0$ = 20 ~ 35 ppm, $[Cl_2]_0$ = 6 ~10 ppm, $[NO]_0$ = 13 ~ 20 ppm

- Product yields were determined after ~20% loss of 1,3-butadiene
- No corrections for secondary reactions

Summary

- The yield of CCA is 35 ± 7 % (± 2σ) in the absence or presence of NO.

- CCA could serve as a “marker” for chlorine atom chemistry in coastal areas.

- CMVK formed in the absence of NO, not in the presence of NO.

Acknowledgements

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