
Reaction monitoring for dehydrohalogenation reactions by IRD

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IRD Application Brief

HP 5965 IRD

IRD 91-5

IRD productivity profile

Industry

Environmental

Chemicals

Trisubstituted chlorobenzene

Sample matrix

Dehydrohalogenation reaction
mixture

Analysis

Isomer differentiation

Introduction

Lindane is a pesticide that has been used throughout the world mainly to combat locusts and other insects. After its deleterious effects were discovered, the world health organization banned the use of lindane. This posed serious disposal problems around the world. The organization which undertook the task of finding an acceptable disposal strategy was the Chemical/Biological Detoxification Branch of the United States Environmental Protection Agency (EPA) in Cincinnati, Ohio. As a result of this EPA work, a safe and very cost-effective method of destruction of this hazardous material was developed. Specifically, lindane was chemically converted into

a useful commercial product. However, the side products of the reaction were isomers which had to be distinguished from the main product. In order to confirm the yield and identity of the useful product, it was important to be able to reliably differentiate between these isomers. The instruments used to perform this task were the HP 5890 GC/5965A IRD and HP 5970B MSD systems. This combination provided a higher confidence qualitative result.

The dehydrohalogenation reaction involves the use of sodium hydroxide and tetraethylene glycol to convert the lindane (a chlorinated cyclic aliphatic hydrocarbon) to three trisubstituted chlorobenzene isomers, shown in Figure 1.

The IRD and MSD chromatograms of these isomers are shown in Figure 2. In order to minimize reaction changes due to elevated temperatures in the chromatographic system, a cool on-column injection technique was utilized.

The 1,2,4-trichlorobenzene is the commercially useful product, and it is present at a substantial reaction yield.

Classification as trisubstituted chlorobenzenes for the compounds in the reaction mixture was immediately established by the MSD, but the three isomers could not be differentiated by this technique alone due to the extreme similarity of their mass spectra, as shown in Figure 3.

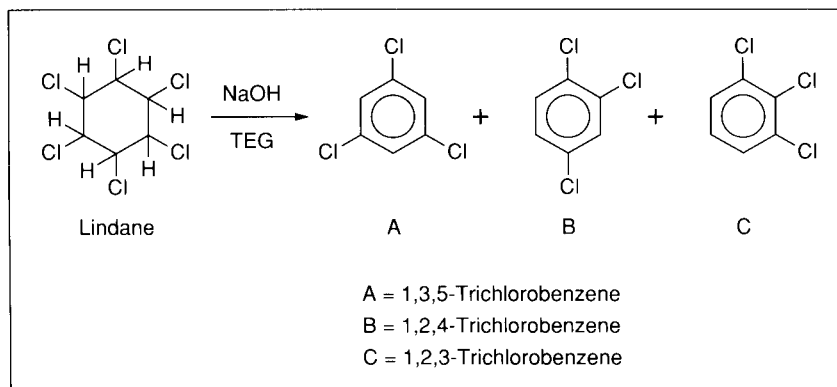


Figure 1. Dehydrohalogenation Reaction

The IRD was able to differentiate the isomers, and thus confirm the high yield of the commercially useful product. The unique, characteristic infrared spectrum of each isomer is shown in Figure 4.

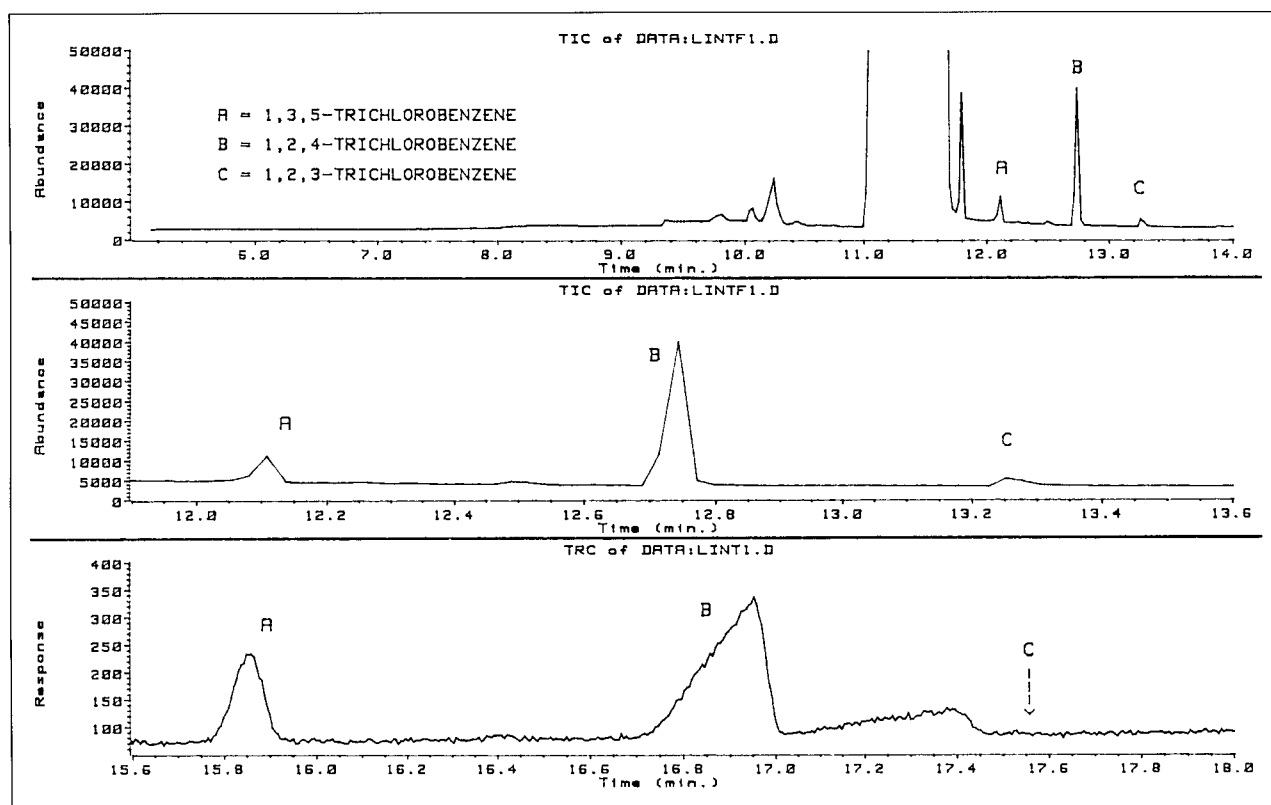


Figure 2.

Conclusion

The optimization of reaction parameters to reduce the yield of the two side products and maximize the yield of the useful product was made easier by monitoring the process with the IRD and MSD combination. This combined system is routinely used in the reaction monitoring of a wide variety of environmentally important halogenated aliphatic and aromatic starting materials. This example demonstrates the powerful ability of the IRD to distinguish between structurally similar compounds. It also illustrates the complimentary nature of MSD and IRD, together providing highly reliable qualitative analysis.

Conditions

Gas chromatograph

Column:

30 m × 0.32 mm ID DB-5 (IRD),
30 m × 0.21 mm ID DB-5 (MSD)
1 micrometer film (IRD),
0.25 micrometer film (MSD)

Carrier gas:

Helium @ 2 ml/min (IRD),
1 ml/min (MSD)

Oven:

40°C (5 min) to 280°C at
10°C/min hold for 10 min

IRD parameters

Light pipe: 280°C

Transfer lines: 280°C

Optical resolution: 8 cm⁻¹,
narrow band MCT
4000–750 cm⁻¹

MSD parameters

Mass range: 40–450 Daltons

Scan rate: 1.06 scans/second

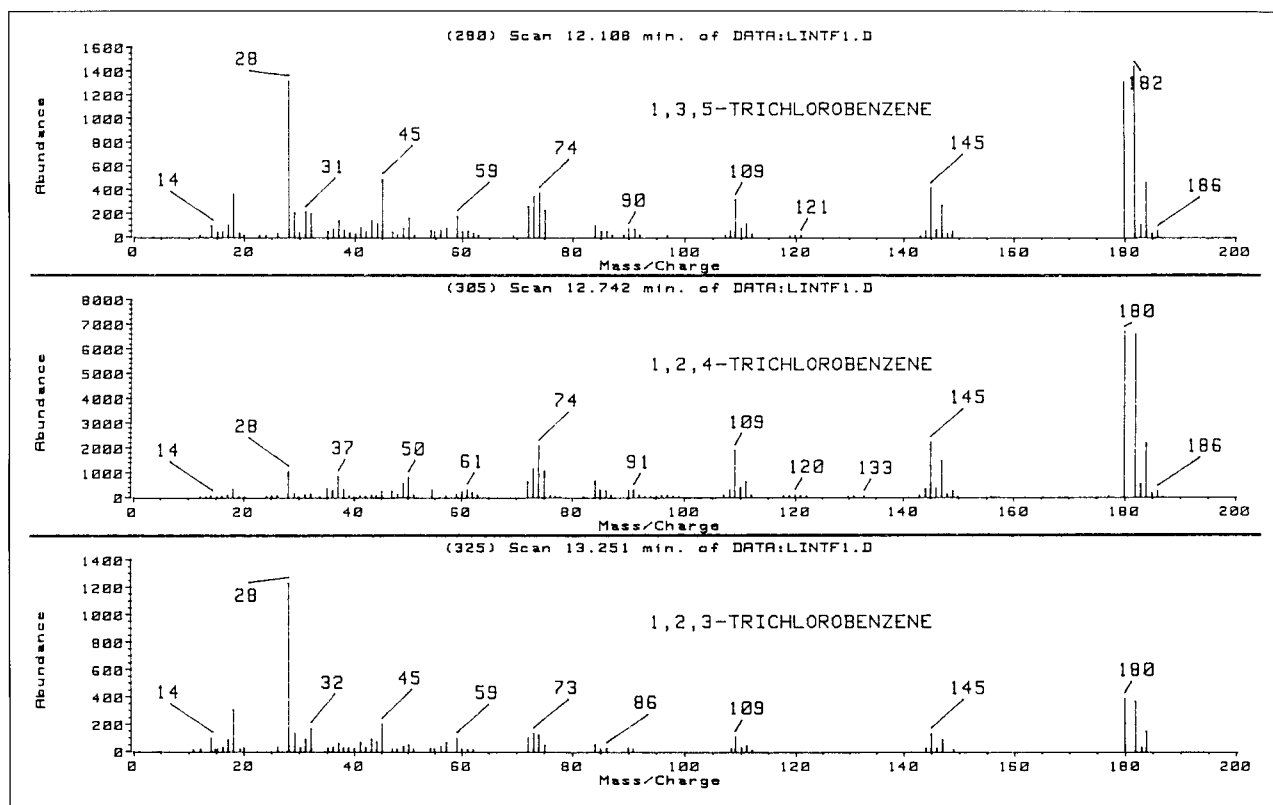


Figure 3.

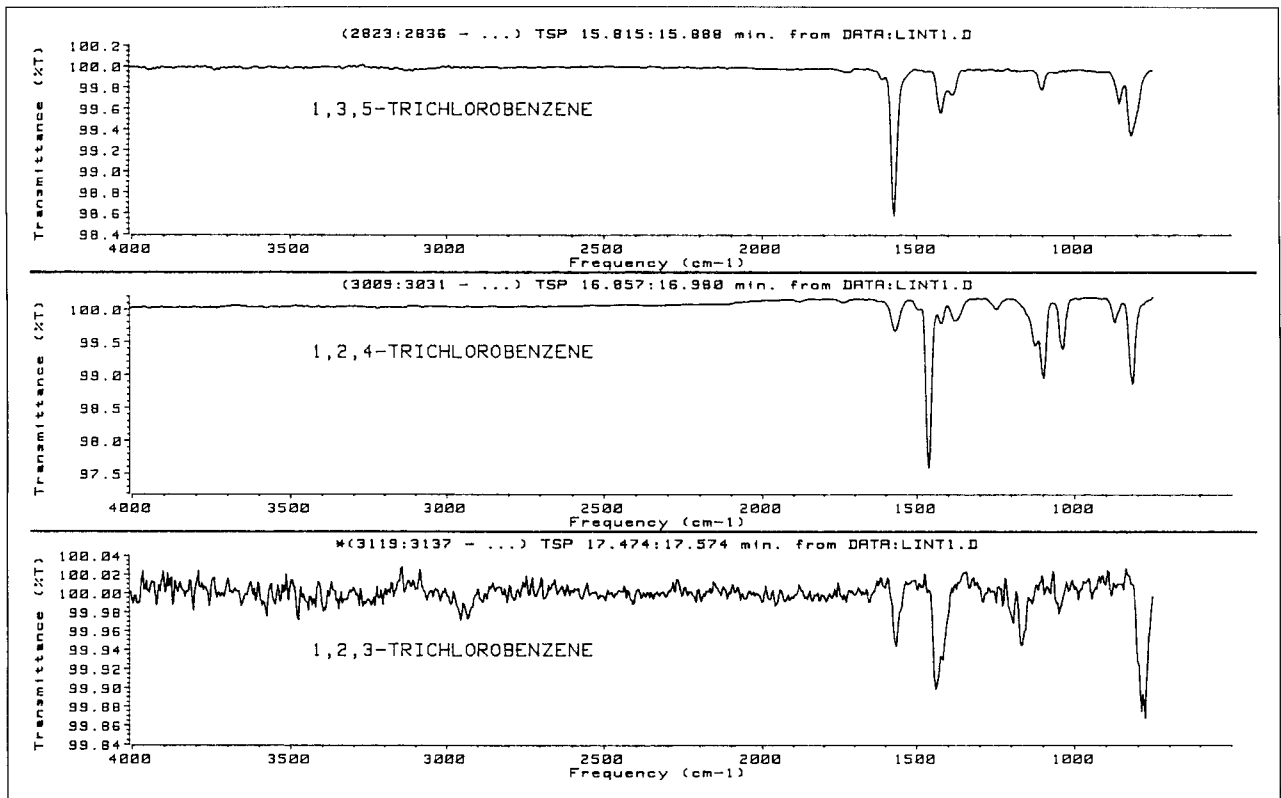


Figure 4.

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