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**Unexpected dimerization of isoprene in a gas chromatography inlet.
A study by gas chromatography/mass spectrometry coupling.**

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ABSTRACT

During analysis of pure isoprene by chromatography/mass spectrometry (GC-MS) using a programmed temperature vaporization (PTV) inlet, the presence of several isoprene dimers was detected in the total ion chromatograms (TICs). This study intends to determine the part of the instrument where dimerization occurs and the relative importance of the dimer amounts under different experimental conditions. The reference thermal dimerization of isoprene gives four six-membered cyclic dimers and two eight-membered ones. In all samples containing different amounts of freshly distilled isoprene, only peaks corresponding to the former appeared in TICs. For the same temperature, their amounts increase as the concentration of injected isoprene increases. The main products are diprene (from 80 to 100%) of the total dimers and dipentene (from 1 to 14%). The sum of the two other dimers is never higher than 6%. In conclusion, isomeric dimers are produced through a dimerization in the inlet. No dimerization of isoprene occurs in the mass spectrometer source. Then care is needed when analyzing terpenic compounds in presence of isoprene by GC-MS because structures, retention times and mass spectra of diprene and dipentene are close.

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