Gas chromatographic analysis of some polyfluorinated alicyclic olefins

In a recent investigation in our laboratory[1] it was necessary that we be able to separate a mixture of the alicyclic olefins $CF_2CF_2CF_2CCl{=}CCl$ (I) b.p. 89°, $CF_2CF_2CF_2CH{=}CCl$ (II) b.p. 77°, $CF_2CF_2CF_2CH{=}CH$ (III) b.p. 72°, and $CF_2CF_2CH_2CCl{=}CF$ (IV) b.p. 87°. In contrast to silicone gum rubber and dinonyl phthalate which gave incomplete resolution of this mixture, excellent separation was obtained employing β,β'-oxydipropionitrile as a liquid phase. The use of β,β'-oxydipropionitrile as a liquid phase for gas chromatographic analyses has been reported in the literature for the separation of hydrocarbons[2,3], alcohols[4], and the esters of the lower fatty acids[5]. Its utility for the separation of polyhalogenated olefins, however, has not been previously reported. This report describes the enhanced separation obtained with β,β'-oxydipropionitrile with the above mixture. Equally satisfactory results have been obtained in our laboratory with mixtures of polyfluorinated cyclobutenes and polyfluorinated acyclic butenes, and the use of β,β'-oxydipropionitrile for the separation of polyfluorinated olefins should find wide utility.

Experimental and results

Dinonyl phthalate (Wilkens Instrument Co.) was used to prepare a 10 % w/w packing on 100–120 mesh Gas-Chrom P (Applied Science Lab.) and packed into an 8 ft. length of 1/4 in. O.D. copper tube and coiled. β,β'-oxydipropionitrile (F&M Scientific Corp.) was used to prepare a 10 % w/w packing on 100–120 mesh Gas-Chrom P and packed into a 10 ft. length of 1/4 in. O.D. copper tube and coiled. A 2 ft. by

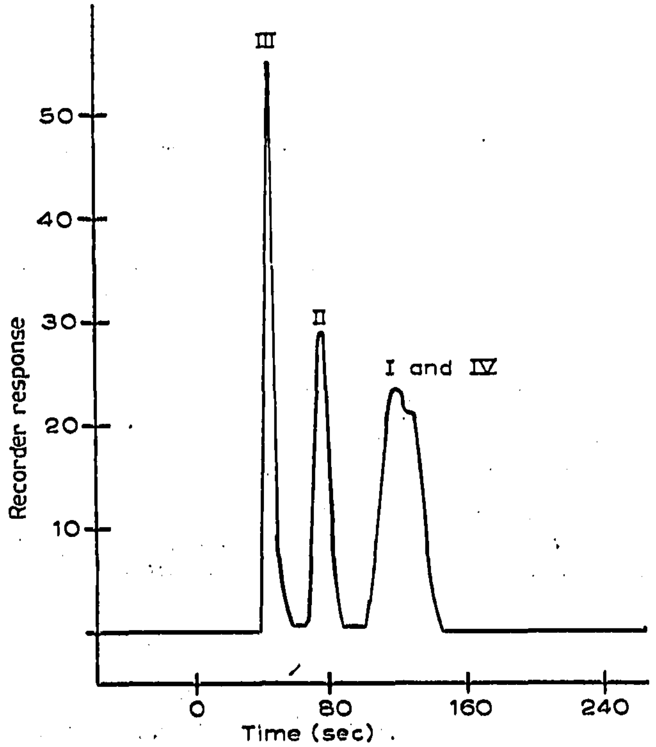

Fig. 1. Chromatogram of olefin mixture on silicone gum rubber.

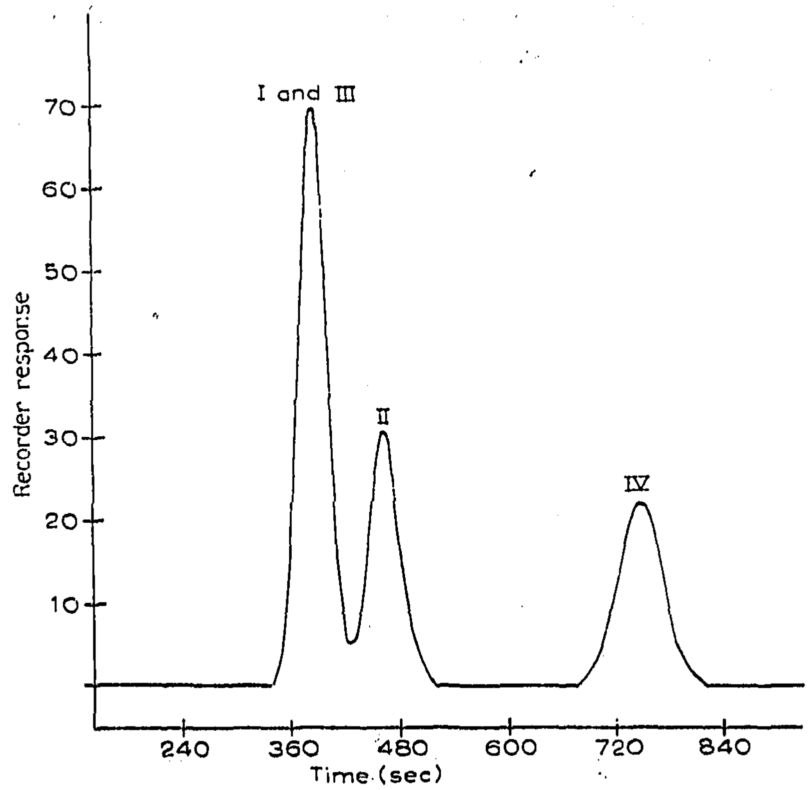

Fig. 2. Chromatogram of olefin mixture on dinonyl phthalate.

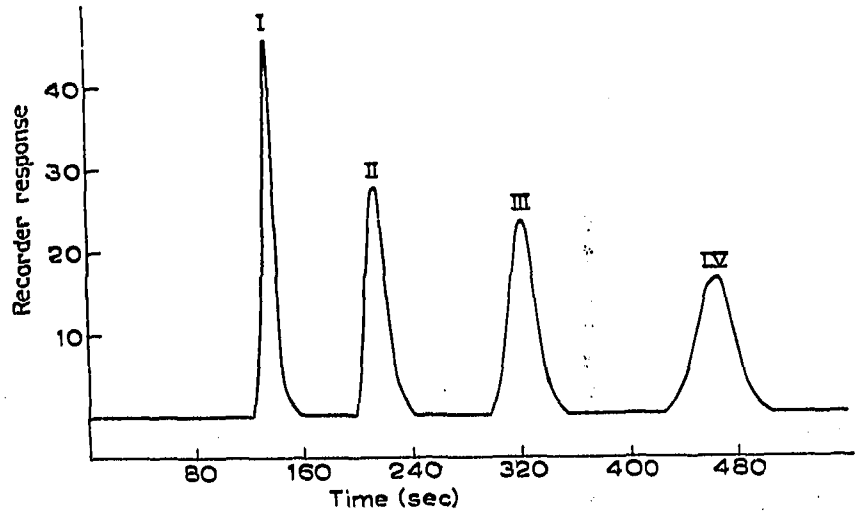

Fig. 3. Chromatogram of olefin mixture on β,β'-oxydipropionitrile.

$^1/_4$ in. O.D. copper column of silicone gum rubber on 60–80 mesh Diatoport-S was obtained from the F&M Scientific Corporation. All chromatograms were obtained on an F&M Model 720 gas chromatograph at 40° and a helium flow rate of 60 ml/min (variation of temperature and flow-rate from these values did not substantially improve the separations). The olefin mixture was approximately equimolar and the sample size was 0.002 ml.

The results of the separations are given in terms of retention times (Table I) and the chromatograms are shown in Fig. 1–3.

TABLE I

RETENTION TIMES OF ALICYCLIC OLEFINS

Column used	*Retention time (sec) of compounds*			
	I	*II*	*III*	*IV*
Silicone gum rubber	120	76	45	120
Dinonyl phthalate	388	476	388	748
β,β'-Oxydipropionitrile	132	212	320	465

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Department of Chemistry, State University of Iowa, Iowa City, Iowa (U.S.A.)

RICHARD L. JOHNSON
DONALD J. BURTON

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Gas chromatography of derivatives of maleic hydrazide

II. Trimethylsilyl maleic hydrazide

The gas chromatographic analysis of maleic hydrazide has been reported earlier to be extremely difficult owing to its extremely high melting point (296–298°)[1]. This same report described the preparation and gas chromatography of alkyl carbonate derivatives of maleic hydrazide.