CHROM. 4235

Gas chromatographic analysis of nitrobenzoic acid isomers

The quantitative determination of isomeric nitrobenzoic acids is accomplished by gas chromatographic separation of the methyl esters on a stationary phase consisting of 10% silicone oil on Celite. The column is operated at 190° with a nitrogen flow rate of 60 ml/min; detection is by flame ionization. Results on synthetic mixtures and on a series of reaction products from the nitration of benzoic acid are discussed.

Experimental

Apparatus and reagents. A Pye 104 series gas chromatograph with flame ionization detector was employed. Peak areas were determined by a Disc Chart Integrator attached to a Honeywell recorder. The column used was a 25 ft. copper coil packed with 10% silicone oil (W. G. Pye & Co., Cambridge) on Celite (80–100 mesh, B.D.H.).

For synthetic samples, *o*-, *m*- and *p*-nitrobenzoic acids supplied by B.D.H. were recrystallized, the *n*-propyl benzoate was used as supplied. Diazomethane required for the methylation was produced by the reaction of sodium hydroxide on *p*-tolylsulphonylmethylnitrosamide, methylation being effected in ether.

Procedure

The nitrobenzoic acids are methylated by treatment with diazomethane in ether. After removal of ether, the esters are weighed together with the requisite amount of *n*-propyl benzoate as internal standard. Sufficient chloroform is then added to effect solution. Aliquots of 0.5 μl are injected onto the column, which is maintained at 190° with a flash heater on the inlet operating at 250°.

The retention times (and detector factors with respect to propyl benzoate) are given in Table I.

TABLE I

RETENTION TIMES AND DETECTOR FACTORS

Component	*Retention time (min)*	*Detector factor (mean of six determinations)*
Chloroform	4	
Methyl benzoate	14	
n-Propyl benzoate	16	1.00 (standard)
Methyl *o*-nitrobenzoate	48	1.88
Methyl *p*-nitrobenzoate	51	1.78
Methyl *m*-nitrobenzoate	54	1.87

Nitration of benzoic acid. One gram of benzoic acid and 10 ml of concentrated sulphuric acid are placed in a thermostated flask fitted with a mechanical stirrer. Five millilitres of a 1:1 mixture of concentrated nitric and sulphuric acids are added over a period of 15 min, such that the temperature remains constant. The reaction mixture is stirred for a further 15 min, then poured onto 500 g of crushed ice and al-

lowed to stand overnight. The precipitated solid is filtered off, washed with cold water and dried.

The filtrate and washings are extracted with 50 ml of chloroform to remove any dissolved nitrobenzoic acids. The reaction product and chloroform are combined, evaporated and dried under vacuum overnight.

TABLE II

ANALYSIS OF SYNTHETIC SAMPLES

	Formulated (%)			*Found* (%)		
	o	*p*	*m*	*o*	*p*	*m* (*by difference*)
Sample 1	4.92	2.57	92.51	4.97	2.46	92.6
				4.53	1.97	93.5
				5.01	2.64	92.3
				4.85	2.45	92.7
Sample 2	1.06	3.22	96.72	1.02	3.28	95.7
				0.94	3.04	96.0
				0.93	3.06	96.0
				1.02	3.26	95.7

TABLE III

NITRATION OF BENZOIC ACID

	Temperature (°C)	*Isomers* (*as percentage of product*)			*Yield* (%)
		o	*p*	*m*	
Nitration 1	5	19.3	1.06	79.7	25
Nitration 2	15	19.5	1.71	78.6	58
Nitration 3	28	19.2	2.33	78.7	>99

Results and discussion

Initial attempts at the separation of methyl nitrobenzoate isomers were made on a 30 ft. column of 10% Apiezon L on Celite. The order of emergence was (a) *ortho*, (b) *meta* and (c) *para* and, although separation could be achieved, small amounts of the *para* isomer, in a sample which was mainly methyl *m*-nitrobenzoate, were masked by the tail of the *meta* peak.

With the silicone oil column the order of emergence is (a) *ortho*, (*b*) *para* and (*c*) *meta*, allowing small quantities of both *ortho* and *para* isomers to be measured in the presence of a large excess of the *meta* isomer, which is the case for the nitration product.

The choice of *n*-propyl benzoate as internal standard allows not only the nitrobenzoates to be quantitatively determined but also the methyl benzoate derived from unreacted benzoic acid, hence a total analysis on the reaction product may be obtained.

Detector factors were obtained for each isomer as the mean result from six chromatograms.

Two synthetic samples were prepared from purified isomers, and analysed to give the results in Table II. From seven of the eight determinations it can be seen that an error of $\pm 5\%$ may be expected on a single result, analyses in triplicate, however, reduce the error to $\pm 2\%$.

Table III shows the isomer analysis of three samples of benzoic acid nitrated at various temperatures. The results in Table II show that this method is capable of yielding a complete isomer analysis of the nitration product unlike the work of ALIPRANDI *et al.*[1], who, using a 6 ft. sodium dodecylbenzene sulphonate column, obtained significant variations in *para* isomer content. This is to be expected when a total area method of calculation is used to determine an isomer which constitutes only 1 % of the sample. The use of an internal standard overcomes this difficulty.

The technique of extracting nitration product washings has been previously ignored although such an omission can obviously lead to inaccuracies due to the varying solubilities of nitrobenzoic acids in aqueous acid solutions.

The results given in Table III (nitration 1) are in agreement with those of HOLLEMAN[2] for *ortho* and *meta* isomers. For the *para* isomer, however, agreement with ALIPRANDI *et al.*[1], who used an isotope dilution analysis technique, would indicate that HOLLEMAN's initial figure is somewhat high. The percentage of the *para* isomer produced is obviously temperature dependent and the procedure described here could be used for kinetic studies on the nitration reaction.

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Received June 9th, 1969