

Gas Chromatographic Analysis of Bromoquinolines

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ABSTRACT

Excellent separations of isomeric bromoquinolines have been obtained using a packed column containing QF-1. The method of analysis was used to assay various products obtained from bromination of quinoline. Observed retention time ranged from 373 sec for quinoline to 1,643 sec for 8-bromoquinoline with respective indexes of 1,596 and 2,018.

INTRODUCTION

The literature reveals little information pertaining to the separation of quinoline derivatives by gas chromatography. Gas chromatography has been used to follow the reaction kinetics of styrylquinoline formation (Lynch and Gordon 1972). The first reported attempt to separate isometric halogenated quinolines was by Goodley and Gordon (1972), who developed a method for the rapid separation and quantitative analysis of selected chlorinated quinolines by gas chromatography.

For separation of the bromoquinolines, the McReynolds (1970) constants indicate that QF-1 would be a good choice and that OV-225 should also be considered. The ability of QF-1 to retard the nitromethane type molecule and the electron donor type molecules seems to involve an interaction between the unshared pair of electrons (quinoline) with the trifluoropropyl group of the liquid phase. Such being the case, retention time should be a function of the electron density at the nitrogen atom. However, it appears from retention data that separation is achieved by a dipole-dipole interaction between the quinoline ring structure and trifluoropropyl group of the liquid phase.

ACKNOWLEDGMENT

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MATERIALS AND METHODS

The liquid phase used was a silicone QF-1 coated onto Chromosorb G, AW, DMCS, 60/70-mesh support and packed into a 10 ft $\times$ 0.093 in (3.04 m $\times$ 0.236 cm), 1/8 in od (0.32 cm) aluminum tube. There was no pretreatment of the support; it was used as received (Johns-Manville Corp.). Of the 5 different liquid loadings tested (range 5–20%), the optimum loading was 10 percent. Other liquid phases, SE-30, OV-225, and Apiezon L, and support materials Chromosorb W, regular; Chromosorb W, DMCS; Chromosorb G, DMCS; and Chromosorb T were found to be ineffective for the separation of the bromoquinolines. Helium was used as a carrier gas for all analyses. The column temperature was 163 C; the injector port temperature was 210 C; the detector temperature was 225 C. Sample size was 0.06 μ l; the carrier gas flow rate was 14.4 ml/min. An effluent splitter located at the column-flame base junction effectively allowed 49 percent (6.6 ml/min) of the effluent to bypass the detector. The remaining 51 percent effluent (7.8 ml/min) entered the hydrogen flame. The recorder used was a Honeywell 1.0 mv full-scale, Model 1630, connected to an Infotronics Digital Integrator, Model CRS-104. The gas chromatograph was a dual channel Varian Aerograph, Model 1520, equipped with flame-ionization detectors.

RESULTS AND DISCUSSION

The retention index values, according to Kovats (1967) and Rohrschneider (1966,

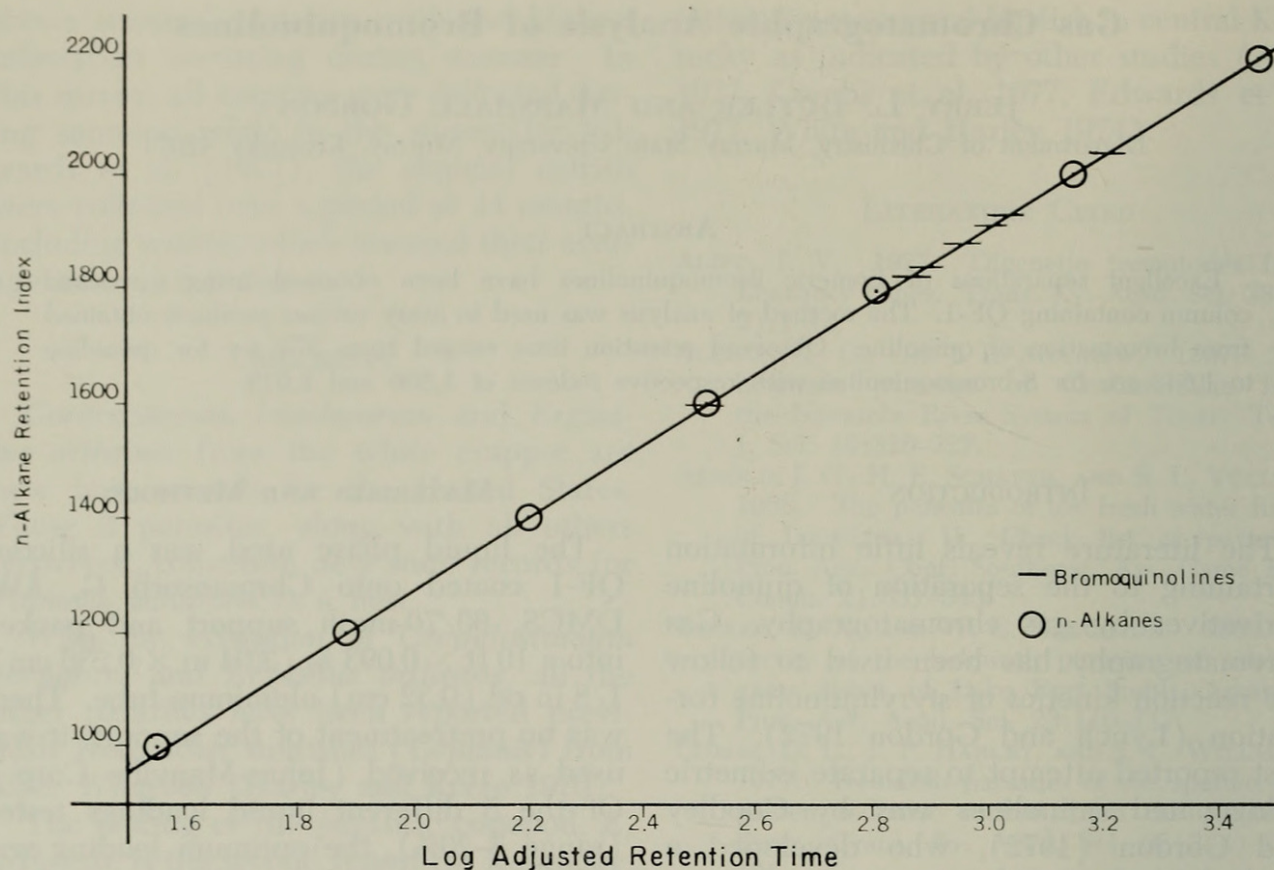


FIG. 1. Plot of log adjusted retention time for the bromoquinoline versus the n-alkane retention index.

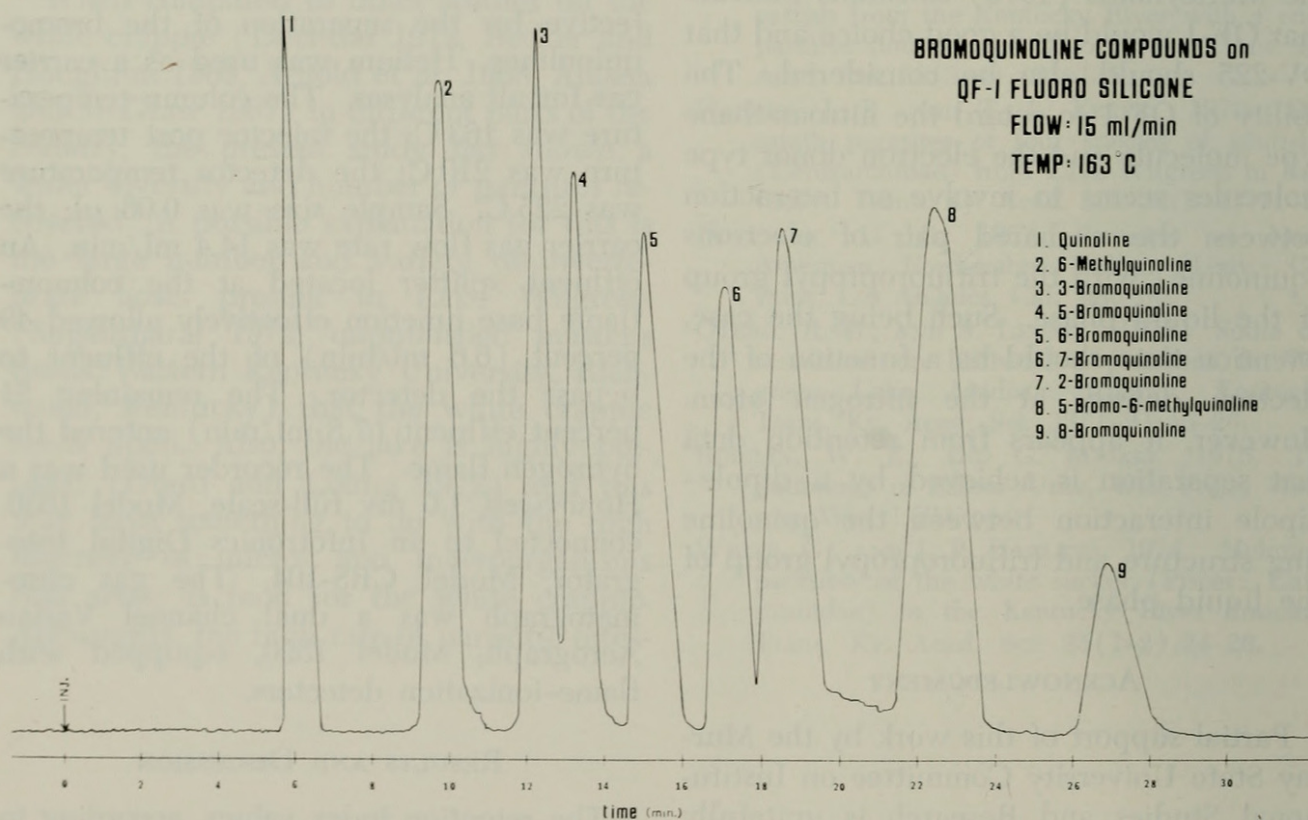


FIG. 2. Typical chromatogram of a standard mixture of the bromoquinoline.

TABLE 1.—RETENTION DATA FOR BROMINATED QUINOLINE ISOMERS ON QF-1 AT 163 C AND 15 ML/MIN FLOW RATE

Compound	Observed retention time (sec)	Adjusted retention time (sec)	Log adjusted retention time	Retention index
methane	37	0	0.0000	100
heptane	48	11	1.0414	700
decane	73	36	1.5563	1,000
dodecane	114	77	1.8865	1,200
tetradecane	199	162	2.2095	1,400
hexadecane	378	341	2.5328	1,600
octadecane	736	699	2.8445	1,800
eicosane	1,469	1,432	3.1559	2,000
docosane	4,982	4,945	3.6942	2,200
quinoline	373	336	2.5263	1,596 ¹
3-bromoquinoline	762	725	2.8603	1,810 ¹
5-bromoquinoline	821	784	2.8943	1,832 ¹
6-bromoquinoline	929	892	2.9504	1,868 ¹
7-bromoquinoline	1,060	1,023	3.0094	1,906 ¹
2-bromoquinoline	1,151	1,114	3.0468	1,930 ¹
8-bromoquinoline	1,643	1,606	3.2055	2,018 ¹

¹ These values were obtained from the equation

$$I = 200 \frac{\log t'_{R1} - \log t'_{Rz}}{\log t'_{R(z+2)} - \log t'_{Rz}} + 100 Z.$$

1967), were found by injecting the normal alkanes into the chromatograph using the same conditions for the bromoquinoline analysis and plotting the log adjusted retention time versus the n-alkane number multiplied by 100 (the n-alkane index) (Fig. 1). Methane was used to obtain a relative reference for the adjusted retention time using the hydrogen flame detector. The conditions for the quinoline isomer analysis were duplicated, using a thermal conductivity detector to establish the fact that air and methane had the same retention time on the QF-1 column. The index values and accompanying data for the QF-1 column at 163 C are shown in Table 1.

Six standard mixtures were made using a wide difference in composition of the quinoline isomers. These mixtures were weighed out on a Mettler balance to the nearest 0.01 mg. Four to 6 injections of each of the 6 standard mixtures were made into the chromatograph, and an average response value for each component was calculated from the observed area of each component. The response factors were calculated on the basis of mole percent composition and related to quinoline as arbitrarily having a response factor of 1.00 (Dietz 1967). The values are shown together with the composition of one of the standards and results from a typical analysis in Table 2.

TABLE 2.—BROMINATED QUINOLINE ANALYSIS AND RELATIVE RESPONSE VALUES ON QF-1 AT 163 C

Compound	Standard (mole percent)	Average analysis (mole percent)	Error	Average response factor
quinoline	22.21	22.37	+0.16	1.00
2-bromoquinoline	11.56	11.45	-0.11	1.10
3-bromoquinoline	13.94	13.85	-0.09	0.99
5-bromoquinoline	11.39	11.45	+0.06	1.04
6-bromoquinoline	12.87	12.72	-0.15	0.99
7-bromoquinoline	14.92	14.90	-0.02	1.05
8-bromoquinoline	13.11	13.16	+0.05	0.98
Total	100.00	100.00		

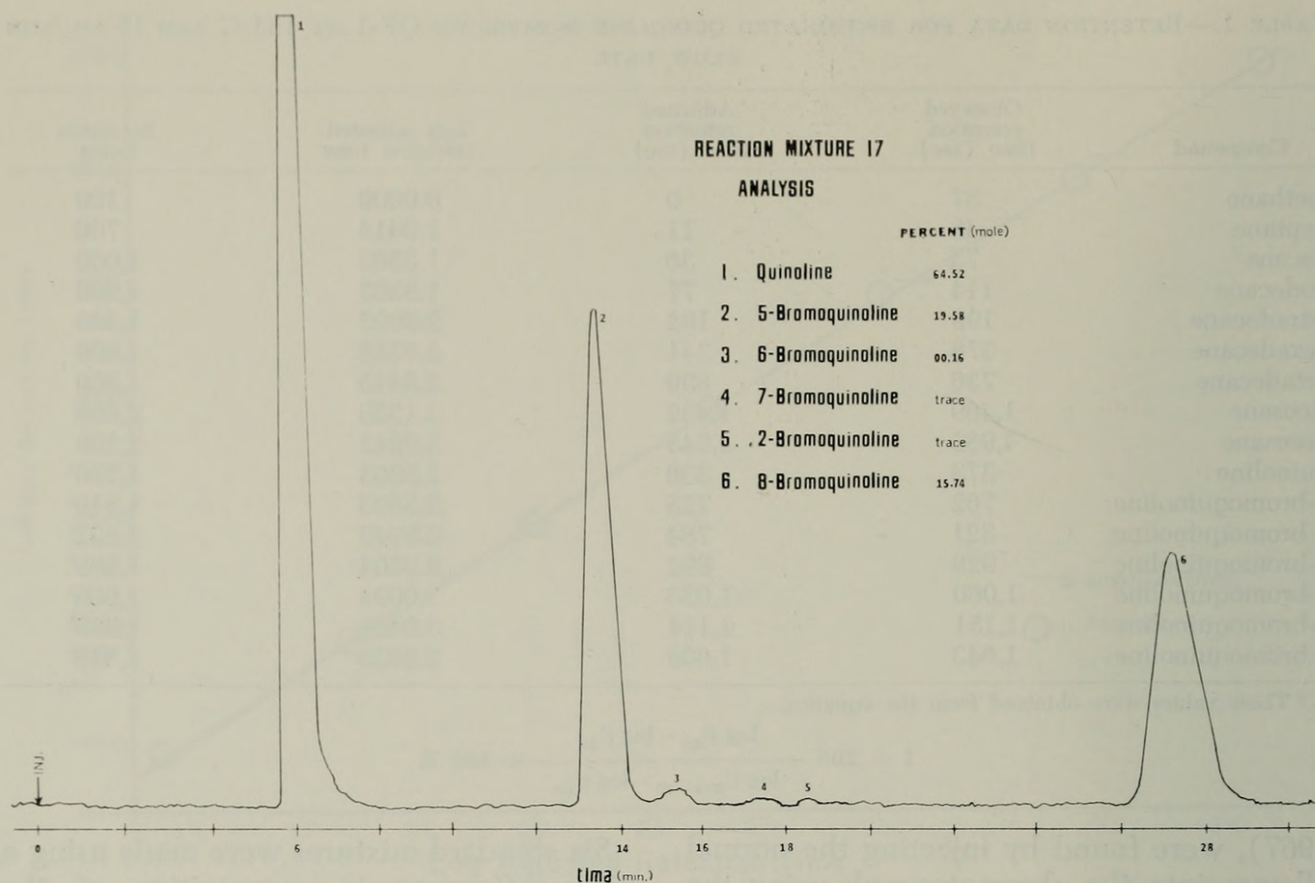


FIG. 3. Typical chromatogram of a bromination reaction mixture.

A discussion of the preparation of bromoquinoline isomers together with details of various bromination reactions conducted is reported elsewhere (Butler and Gordon 1975).

The brominated quinoline reaction mixtures were analyzed in the same way as the standard mixtures. The mole percent of each isomer present was calculated from the product of the area obtained and the response factor for that isomer. In some analyses, there was a rise in the baseline of the chromatograph recording, but the area was not sufficient for the electronic integrator to respond. For those instances, the isomers present, in obviously small amounts, were indicated as "trace." Figs. 2 and 3 illustrate chromatograms of a standard mixture and a reaction mixture, respectively.

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