



ELSEVIER

Short communication

# Separation and determination of reaction mixtures of anthraquinone by gas chromatography<sup>☆</sup>

Sajid Husain\*, P. Nageswara Sarma, K. Sita Rama Rao, V.V.S. Lakshmi

*Analytical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India*

First received 8 March 1994; revised manuscript received 26 July 1994

## Abstract

Anthraquinone is a valuable organic intermediate commonly prepared by the reaction of phthalic anhydride with benzene and subsequent acid cyclization of the product obtained. Rapid, sensitive and selective analytical methods are essential for monitoring the reactions during process development. A gas chromatographic method using an internal standard is described for the separation and determination of the reaction products obtained during the manufacture of anthraquinone.

## 1. Introduction

Anthraquinone is a valuable intermediate in the manufacture of dyestuffs and pigments [1] and several methods are available for its preparation. It is generally prepared by the reaction of phthalic anhydride with benzene [2,3] in the presence of a catalyst to give *o*-benzoylbenzoic acid, followed by acid cyclization. Process development for the manufacture of anthraquinone starting from phthalic anhydride and benzene is in progress in our institute. During the process, selective, accurate and rapid analytical methods are required for monitoring the reactions.

A literature search revealed that anthraquinone has been determined in different matrices [4–11] using various instrumental techniques. It has been determined as a by-product in the preparation of benzaldehyde by gas chromatog-

raphy (GC) [12]. However, no method has been reported for the separation and determination of components of reaction mixtures during the preparation of anthraquinone from phthalic anhydride. This prompted us to undertake the present studies.

A rapid, selective and precise GC method with acenaphthene as an internal standard was developed for the analysis of reaction mixtures obtained during the preparation of anthraquinone from phthalic anhydride.

## 2. Experimental

### 2.1. Materials

Acenaphthene was procured from Fluka (Buchs, Switzerland). Phthalic anhydride, benzophenone and anthraquinone were purchased from Loba Chemicals (Bombay, India). OV-17 used as the stationary phase and Chromosorb W

\* Corresponding author.

<sup>☆</sup> ICT Communication No. 3357.

AW used as an inert support were obtained from Analabs (North Haven, CT, USA). All other chemicals and solvents were of analytical reagent grade.

## 2.2. Gas chromatography

A Hewlett-Packard Model 5840A gas chromatograph provided with a flame ionization detector equipped with a microprocessor was used under the following conditions: 15% OV-17 on Chromosorb W AW (80–100 mesh); column, stainless-steel (6 ft. × 1/8 in. I.D.); column temperature, 250°C; injection port temperature, 300°C; detector temperature, 300°C; chart speed, 1 cm/min; carrier gas, nitrogen; flow-rate, 45 ml/min; and injection volume, 1  $\mu$ l.

## 2.3. Preparation of standard mixtures

Standard mixtures were prepared in the same proportions as expected in the reaction mixtures using acenaphthene as internal standard. Standard mixtures of various compositions were

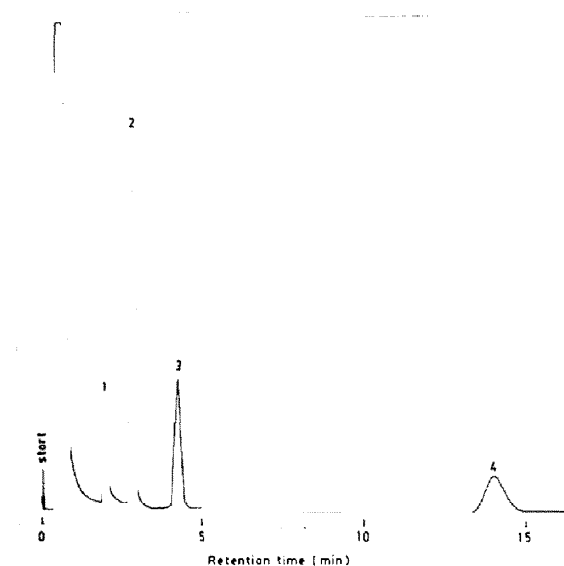


Fig. 1. Typical gas chromatogram showing the separation of a standard mixture of (1) phthalic anhydride, (3) benzophenone and (4) anthraquinone, with (2) acenaphthene as internal standard.

Table 1

Relative retention times (RRT) and relative response factors (RRF) of phthalic anhydride, anthraquinone and benzophenone on OV-17 stationary phase

Compound	RRT	RRF
Phthalic anhydride	0.68	2.56
Anthraquinone	5.01	1.24
Benzophenone	1.49	1.11
Acenaphthene (internal standard)	1.00	1.00

prepared. Triplicate runs were made for each standard mixture and reaction mixtures.

## 3. Results and discussion

The separation of anthraquinone, benzophenone and phthalic anhydride was studied on various stationary phases. It was found that the resolution was very good on 15% OV-17. A typical chromatogram showing the separation of phthalic anhydride, anthraquinone and benzophenone in a standard mixture containing an internal standard is depicted in Fig. 1. The elution sequence follows the order phthalic anhydride, benzophenone and anthraquinone, which has been confirmed by injecting authentic samples.

The relative retention times and relative response factors of these compounds with respect

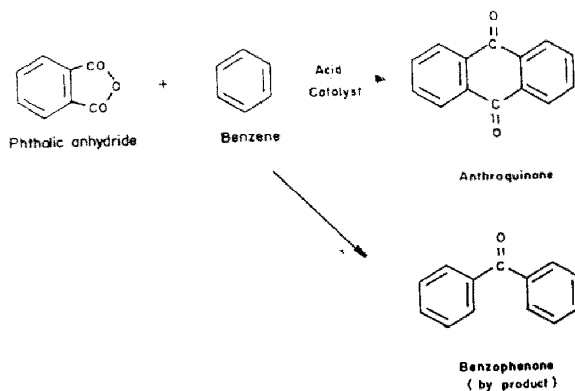


Fig. 2. Reactions for the preparation of anthraquinone.

Table 2  
Results of the analysis of standard mixtures of phthalic anhydride, anthraquinone and benzophenone by GC

Compound	Mixture No.				
	1	2	3	4	5
<b>Phthalic anhydride</b>					
Taken (%)	49.40	32.58	29.53	32.06	8.57
Found (%)	49.99	31.78	28.85	31.40	8.24
Standard deviation ( <i>n</i> = 3)	0.395	0.217	0.310	0.488	0.143
<b>Anthraquinone</b>					
Taken (%)	17.68	40.34	29.07	26.94	62.24
Found (%)	18.17	41.34	29.64	26.43	60.79
Standard deviation ( <i>n</i> = 3)	0.361	0.481	0.209	0.283	0.671
<b>Benzophenone</b>					
Taken (%)	10.73	8.20	25.28	17.14	9.18
Found (%)	10.62	8.30	25.22	16.75	9.48
Standard deviation ( <i>n</i> = 3)	0.169	0.008	0.129	0.215	0.103

to acenaphthene (internal standard) are given in Table 1. The relative response factors of phthalic anhydride, benzophenone and anthraquinone are >1, which indicates that the detector response is not 100%. The efficiency of the method was tested with various synthetic mixtures. The results obtained are given in Table 2. It can be observed from Table 2 that the experimental values are in good agreement with the true values and are within the limits of experimental error.

The method of preparation of anthraquinone from phthalic anhydride and benzene is shown in Fig. 2. A number of reaction mixtures obtained during the preparation of anthraquinone were analysed by the developed method and the results are given in Table 3.

A typical gas chromatogram showing the separation of reaction mixtures of anthraquinone is given in Fig. 3. It can be seen that an additional peak is obtained at 5.98 min, and GC-MS was applied to identify this peak. It was concluded

Table 3  
Results of the analysis of typical reaction mixtures of anthraquinone

Mixture No.	Phthalic anhydride (%)	S.D. ( <i>n</i> = 3)	Anthraquinone (%)	S.D. ( <i>n</i> = 3)	Benzophenone (%)	S.D. ( <i>n</i> = 3)
1	45.94	0.261	2.36	0.068	16.59	0.014
2	30.33	0.300	8.89	0.090	3.41	0.032
3	27.72	0.202	7.68	0.028	3.56	0.012
4	8.96	0.270	6.48	0.032	2.03	0.040
5	8.04	0.290	3.33	0.043	2.27	0.007

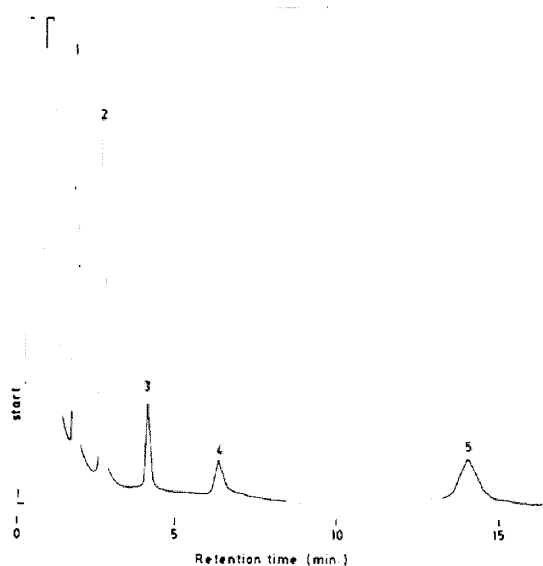


Fig. 3. Typical gas chromatogram showing the separation of anthraquinone reaction mixture. Peaks: 1 = phthalic anhydride; 2 = acenaphthene (internal standard); 3 = benzophenone; 4 = unidentified; 5 = anthraquinone.

that it may be 9-fluorenone. The total time for the analysis was 30 min.

#### Acknowledgements

The authors thank Dr. A.V. Rama Rao, Director, IICT, for his keen interest and encourage-

ment. They also thank Dr. M. Subrahmanyam and Dr. V. Durgakumari, IICT, for supplying reaction mixtures.

#### References

- [1] A.J. Confrancesco, in M.H. Grant (Editor), *Encyclopedia of Chemical Technology*, Vol. 2, Wiley, New York, 4th ed., 1992, p. 801.
- [2] H. Sadamori and T. Okazaki, *Jpn. Pat.*, 74 95 952 (1974); *Chem. Abstr.*, 82 (1975) 43097p.
- [3] G. Friedhofen, O. Immel and H. Schwarz, *Ger. Pat.* 2 633 458 (1978); *Chem. Abstr.* 88 (1978) 137904j.
- [4] P.P. Rai, T.O. Turner and S.A. Maltin, *J. Chromatogr.*, 110 (1975) 401.
- [5] F. Tsutomu, S. Shoji and L. Hidefume, *J. Chromatogr.*, 21 (1966) 116.
- [6] Y.A. Tang and W.A. Aue, *Mikrochim. Acta*, 2 (1987) 21; *Chem. Abstr.*, 109 (1988) 16399s.
- [7] M. Coskun, *Int. J. Pharmacogn.*, 30 (1992) 151; *Chem. Abstr.*, 117 (1992) 258328a.
- [8] V. Stepan and V. Vodehnal, *Collect. Czech. Chem. Commun.*, 36 (1971) 3964; *Chem. Abstr.*, 76 (1972) 78720y.
- [9] L.Y. Kheifet and V.D.B. Bezuglyi, *Org. Poluprod. Krasiteli*, (1969) 164; *Chem. Abstr.*, 72 (1970) 62117p.
- [10] J.P. Hans, *J. Chromatogr.*, 26 (1967) 515.
- [11] H. Thielemann, *Sci. Pharm.* 40 (1972) 291; *Chem. Abstr.*, 78 (1973) 75917y.
- [12] G.D. Mitra and S.K. Ghosh, *Fert. Technol.*, 17 (1980) 194; *Chem. Abstr.*, 96 (1982) 154747t.