

## Note

### Gas chromatographic behaviour of several *p*-quinones

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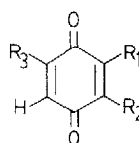
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Several functional groups, two carbonyls and two double bonds in a six-membered ring, are present in the structure of quinones. Though gas chromatography (GC) has been used to analyze different kinds of quinones, *e.g.*, refs. 1 and 2, we could find no studies of the chromatographic behaviour of the *p*-quinones which we wished to examine (see Scheme 1).

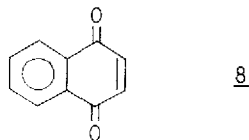
#### p-QUINONES

##### A. *p*-benzoquinones

	<u>R<sub>1</sub></u>	<u>R<sub>2</sub></u>	<u>R<sub>3</sub></u>
<u>1</u>	H	H	H
<u>2</u>	CH <sub>3</sub>	H	H
<u>3</u>	CH <sub>3</sub>	H	CH <sub>3</sub>
<u>4</u>	tBu	H	tBu
<u>5</u>	OCH <sub>3</sub>	H	H
<u>6</u>	OCH <sub>3</sub>	H	OCH <sub>3</sub>
<u>7</u>	H	OCH <sub>3</sub>	CH <sub>2</sub> OH



##### B. 1,4-naphthoquinone

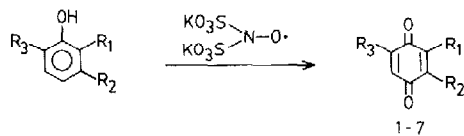


Scheme 1.

The objectives of the present study were: (i) to determine Kováts retention indices, *I*, for seven *p*-benzoquinones and one naphthoquinone on several packed columns at different temperatures; (ii) to study the influence of column temperature, *t*, and polarity, *P*, of the stationary phase on the chromatographic behaviour of these eight compounds.

## EXPERIMENTAL

The seven *p*-benzoquinones (1-7) were prepared by oxidation of the corresponding phenols with potassium nitrosodisulphonate (Fremy's salt)<sup>3,4</sup>, see Scheme 2. The naphthoquinone (8) was supplied by Merck.



Scheme 2.

All the products were characterized by IR and <sup>1</sup>H NMR spectroscopy and by comparison of their melting points with those in the literature<sup>3,4</sup>.

Retention indices, *I*, for the compounds were determined using a Perkin-Elmer Sigma 2B chromatograph equipped with an Hewlett-Packard Model 3390A integrator and/or a Hewlett-Packard Model 5830A chromatograph equipped with a Model 18850A integrator and a flame ionization detector. The commercially available packing materials SE-30, OV-17, UCON 50 LB 550X, poly(phenyl ether), XE-60, Carbowax 20M and diethylene glycol succinate (DEGS) were supplied by Teknokroma (Barcelona, Spain). The stationary phases and conditions used are shown in Table I.

All the sample quinones were injected as solutions (1.0-2.0 μl) in diethyl ether (5-10%, w/w). Retention times were measured from the times of sample injection. The dead volume was determined by regression analysis by use of a series of C<sub>8</sub>-C<sub>24</sub> *n*-alkanes and the Gröbler-Bälizs<sup>6</sup> procedure.

## RESULTS AND DISCUSSION

Retention indices, *I*, of compounds 1-8 on different stationary phases are shown in Table II. On a given stationary phase, quinones with similar molecular

TABLE I  
EXPERIMENTAL CONDITIONS AND DIFFERENT STATIONARY PHASES STUDIED

Columns: 2 m × 1/8 in. (1, 5-7) and 2 m × 1/4 in. (2-4). Support: Chromosorb P AW DMCS (60-80 mesh). Injection temperature: 250°C. Detector temperature: 250°C. Carrier gas (nitrogen) flow-rate: 20 ml/min (1, 5-7) and 30 ml/min (2-4).

No.	Stationary phase	Polarity <sup>5</sup>	Column temperatures (°C)
1	SE-30	6.8	180, 190, 200, 210, 220
2	OV-17	27.4	140, 150, 160, 170, 180
3	UCON 50 LB 550X	31.2	140, 150, 160, 170, 180, 190
4	Poly(phenyl ether) (PPE)	37.0	160, 170, 180, 190
5	XE-60	53.8	180, 190, 200, 210
6	Carbowax 20M (CW 20M)	70.8	180, 190, 200, 210
7	DEGS	108.5	160, 170, 180, 190

TABLE II  
 RETENTION INDICES,  $I$ , FOR THE  $p$ -QUINONES STUDIED

Column	$t$ ( $^{\circ}\text{C}$ )	Quinone								
		1	2	3	4	5	6	7	8	
SE-30	180	905	1008	1113	1468	1220	1506	1540	1410	
	190	912	1015	1119	1474	1228	1515	1549	1418	
	200	919	1018	1125	1480	1234	1522	1562	1427	
	210	923	1025	1130	—	1240	1530	1573	1437	
	220	—	1031	—	1489	—	—	—	1444	
		$\Delta I_j^{\circ}\text{C}^*$	0.60	0.58	0.57	0.53	0.66	0.80	1.10	0.85
	$r^*$	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
OV-17	140	1151	—	—	1609	1560	—	—	—	
	150	1156	1244	1338	—	1566	—	—	—	
	160	1163	1250	1343	1618	1573	1651	—	1715	
	170	1169	1257	—	—	—	1658	—	1724	
	180	1175	1260	1354	—	1585	1666	1854**	1732	
	190	—	—	—	1633	—	1675	1869	—	
	200	—	—	1367	1636	1600	1683	1876	1757	
	210	—	1279	—	—	—	—	1885	—	
		$\Delta I_j^{\circ}\text{C}$	0.60	0.58	0.58	0.45	0.67	0.80	1.03	1.05
	$r$	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
Poly(phenyl ether)	160	1287	1383	1480	1675	—***	—***	—***	—	
	170	1293	1390	1485	1682	—	—	—	1883	
	180	1299	1395	1490	1687	—	—	—	1889	
	190	1305	1400	1496	1692	—	—	—	1903	
		$\Delta I_j^{\circ}\text{C}$	0.60	0.57	0.53	0.57	—	—	—	1.00
	$r$	1.00	0.99	0.99	0.99	—	—	—	0.97	
UCON 50 LB 550X	140	1241	1303	1392	1609	—***	—***	—***	—	
	150	1248	1310	1400	1613	—	—	—	1812	
	160	1256	1317	1406	1620	—	—	—	1827	
	170	1262	1323	1411	1626	—	—	—	1831	
	180	—	1330	1417	1633	—	—	—	1848	
	190	—	1337	1422	—	—	—	—	1865	
		$\Delta I_j^{\circ}\text{C}$	0.70	0.68	0.60	0.60	—	—	—	1.33
		$r$	0.99	1.00	0.99	0.99	—	—	—	0.98
XE-60	180	1469	1545	1632	1826	2001	—***	2078	2066	
	190	1486	1566	1651	1842	2026	—	2099	2093	
	200	1509	1588	1671	1858	2043	—	2118	2120	
	210	1527	1602	1687	1872	2066	—	2145	2146	
		$\Delta I_j^{\circ}\text{C}$	1.93	1.90	1.83	1.53	2.17	—	2.23	2.67
		$r$	0.99	0.99	0.99	1.00	0.99	—	0.99	1.00
Carbowax 20M	180	1562	1616	1681	1809	—***	—***	—***	2205	
	190	1570	1624	1686	1814	—	—	—	2216	
	200	1579	1633	1695	1820	—	—	—	2228	
	210	1587	1640	1703	1824	—	—	—	—	
		$\Delta I_j^{\circ}\text{C}$	0.83	0.80	0.73	0.50	—	—	—	1.15
	$r$	1.00	0.99	0.99	0.99	—	—	—	1.00	

(Continued on p. 308)

TABLE II (continued)

Column	$t$ (°C)	Quinone							
		1	2	3	4	5	6	7	8
DEGS	160	1917	1959	2014	2036	—***	—***	—***	2544
	170	1954	1994	2048	2065	—	—	—	2588
	180	1983	2023	2084	2098	—	—	—	2645
	190	2016	2055	2106	2118	—	—	—	2685
	$\Delta I_i^\circ\text{C}$	3.30	3.20	3.07	2.73	—	—	—	4.70
	$r$	0.99	1.00	0.99	0.99				0.99

\* Slope,  $\Delta I_i^\circ\text{C}$ , and correlation coefficient,  $r$ , of the linear relationship  $I$  vs.  $t$  (°C).

\*\* The isomeric compound 2-hydroxymethyl-6-methoxy-*p*-benzoquinone of 7 (Scheme 1) has only been characterized on this stationary phase:  $t = 180^\circ\text{C}$ ;  $I = 2004$ .

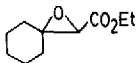

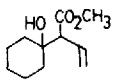

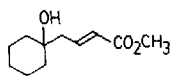



\*\*\* This compound was not detected under the experimental conditions used.

weights present higher values of  $I$  when the substituents have higher polarities, *i.e.*, in the order  $1 < 2 < 5$  where  $R_1 = \text{H}$ ,  $\text{CH}_3$  and  $\text{OCH}_3$ , or  $6 < 7$  because  $\text{OCH}_3$  is less polar than  $\text{CH}_2\text{OH}$ .

High values of  $\Delta I_i^\circ\text{C}$  are generally characteristic of cyclic systems<sup>7-10</sup>. The present *p*-quinones exhibit such behaviour (see Table III). On the other hand, when the number of non-polar acyclic substituents of the *p*-benzoquinone increases or when the acyclic substituents are larger, a decrease in  $\Delta I_i^\circ\text{C}$  is produced, *i.e.*, in the order

TABLE III

 $\Delta I_i^\circ\text{C}$  FOR DIFFERENT CYCLIC SYSTEMS ON UCON 50 LB 550X PHASES

No.	Compound	$\Delta I_i^\circ\text{C}$	No.	Compound	$\Delta I_i^\circ\text{C}$
1		0.5 <sup>10</sup>	5		1.1 <sup>10</sup>
2		1.0*	6		0.95 <sup>9</sup>
3		1.0*	7		0.90
4		1.3 <sup>10</sup>	8		1.33

\* Retention indices: compound 2, 1395 (220), 1405 (230), 1415 (240°C); compound 3, 1575 (220), 1586 (230), 1595 (240°C). Carrier gas: nitrogen; flow-rate 37 ml/min. Other conditions as described in Experimental.

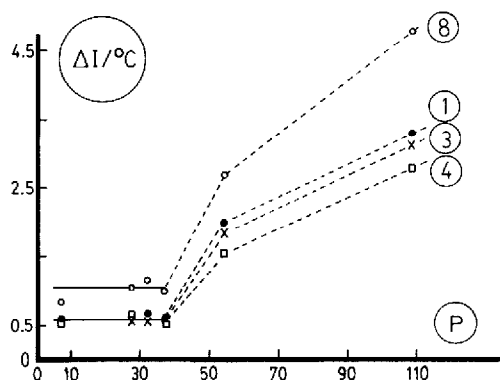


Fig. 1. Change in retention index (for compounds 1, 3, 4 and 8 from Scheme 1) with respect to temperature,  $\Delta I/^\circ\text{C}$ , vs. polarity,  $P$ , for the stationary phases SE-30, OV-17, UCON 50 LB 550X, poly(phenyl ether) (PPE), XE-60 and DEGS (see Table I).

$4 < 3 < 2 < 1$ . The introduction of polar acyclic substituents results in higher  $\Delta I/^\circ\text{C}$  values, thus  $1 < 5 < 6 < 7$ . Finally when the number of cyclic rings increases,  $\Delta I/^\circ\text{C}$  increases, *i.e.*,  $1 < 8$ .

Though the number of compounds is too small for definitive conclusions, it does appear that  $\Delta I/^\circ\text{C}$  is constant on stationary phases with low polarity ( $P < 40$ ), see Fig. 1, and increases with increasing polarity of the stationary phase (see Fig. 1).

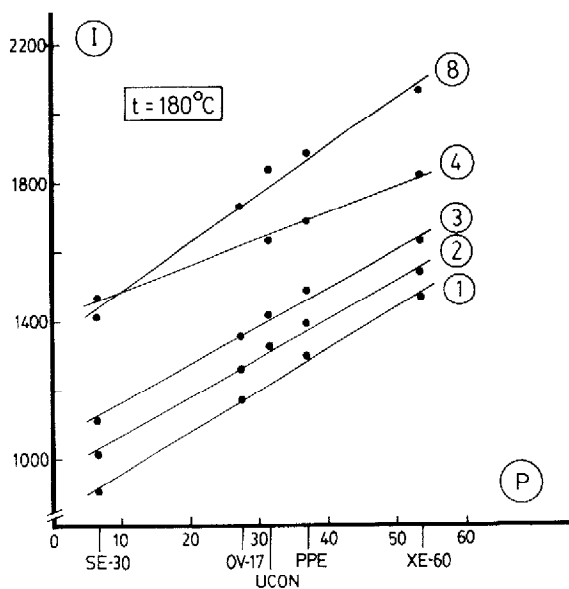
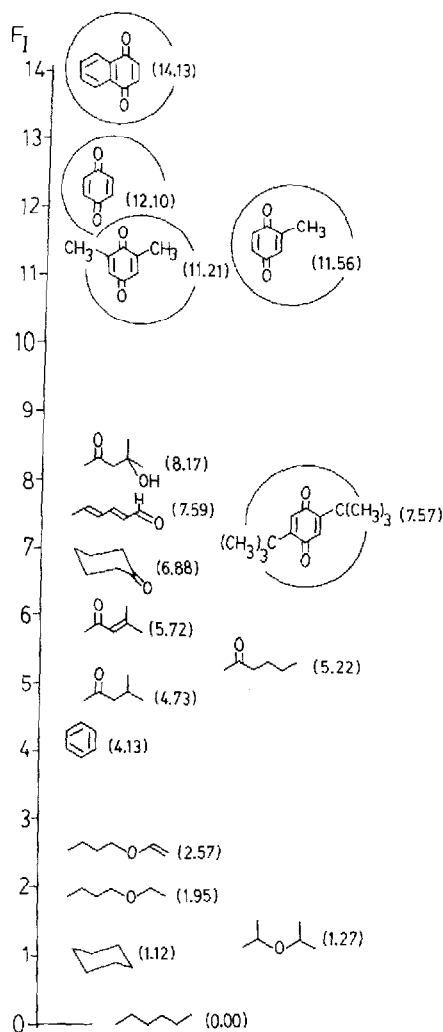


Fig. 2. Plots of retention index,  $I$ , for compounds 1-4 and 8 (from Scheme 1) vs. stationary phase polarity,  $P$ .



Scheme 3.

Carbowax 20M shows an anomalous behaviour, as with other compounds studied on this stationary phase\* with smaller  $\Delta I_i/^\circ\text{C}$  values (see Table II).

The influence of the stationary phase on the chromatographic behaviour of *p*-quinones can be observed in Fig. 2 where straight lines,  $I$  vs.  $P$ , with correlation coefficients  $\geq 0.98$  are obtained for stationary phases with  $P < 60$ .

In order to study the influence of the molecular structure of the solute and the polarity of the stationary phase, the slopes,  $F_1$ , of the plots of  $I$  vs.  $P$  were studied for the alkyl-*p*-benzoquinones (1-4) and 1,4-naphthoquinone (8) and compared with those for other cyclic and acyclic compounds<sup>1,2</sup> (see scale of  $F_1$  values in Scheme 3).

\* OTMS derivatives of aldopentoses and aldohexoses show an anomalous behaviour on Carbowax 20M<sup>11</sup>.

In a previous paper<sup>12</sup>, the influence of the polarity of the stationary phase was studied. Different kinds of compounds (alkanes, cycloalkanes, ethers, esters, aldehydes, ketones and aromatic hydrocarbons) were investigated and in all cases the graphs of  $I$  vs.  $P$  (polarity of the stationary phase) are straight lines with high correlation coefficients (0.96–1.00). The results show that higher values of  $F_I$  are obtained when higher numbers of functional groups or more polar groups are present in the compound.

In Scheme 3 it is seen that the quinones have the highest  $F_I$  values compared to those of the other compounds. This is in agreement with the number of functional groups (two C=O and two C=C in a cyclic system) present in the molecule. However, 2,5-di-*tert.*-butyl-*p*-benzoquinone (4) has the lowest  $F_I$  value, in accord with the presence of the two alkyl groups.

Finally, we propose the use of columns packed with dimethylpolysiloxane, *i.e.*, SE-30, or methylphenylpolysiloxane, *i.e.*, OV-17, for the studies of the *p*-benzoquinones. On these stationary phases all the *p*-quinones studied in this paper can easily be separated and characterized in less than 60 min.

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