

Notes

A reaction occurring between benzoin and quinone on a gas chromatographic column

During the course of a systematic study of the behaviour of benzoin and various substituted benzoin on gas chromatographic columns (to be published at a later date), a mixture of benzoin and *p*-benzoquinone in methyl ethyl ketone was injected into a column. The peaks that were detected besides the solvent consisted of hydroquinone, deoxybenzoin, and benzil. Quinone itself was never detected even after 23 min at 182°. (This in itself is a little surprising as quinone is relatively volatile.) Mixture solutions of varying concentrations were used and the sample size in all cases was 40 μ l. The hydroquinone peak appeared on the tail of the solvent peak and was sharp and symmetrical allowing for its position. Authentic samples of hydroquinone had retention times slightly shorter, 1.85–1.90 min, than the produced hydroquinone, 1.95–2.05 min.

Benzoin itself on injection into a column gives only deoxybenzoin and benzil with no benzoin at all coming out. At 182° the molar ratio benzil/deoxybenzoin is 2.0 for an injection of only benzoin. This ratio increases with the amount of quinone present. No reaction occurred between the benzoin and quinone in the cold solution. However, on heating approximately 1/1 molar mixture of benzoin and quinone to 190° in a sealed evacuated tube (10⁻³ mm Hg) a reaction was seen with the mixture turning black. The IR spectrum of a solution of the product in methyl ethyl ketone gave a peak at 828 cm⁻¹ ascribable to neither benzoin, quinone or solvent but also given by a solution of hydroquinone. Pure quinone itself, and pure benzoin itself under the same conditions, underwent no changes. Visual inspection of the column after injections of quinone-benzoin mixtures showed progressive blackening of the first few cm, with most of the blackening on the glass wool plug immediately above the packing. After injection of a sample containing quinone it took two successive injections of benzoin solution for the benzil-deoxybenzoin ratio to return to its usual value for that column.

Experimental

The gas chromatograph used was Burrell model K-1 with its new type thermal conductivity detector at 200°. The column used was 250 cm long and filled with 20 % Dow Corning high vacuum grease on 80–100 mesh Chromosorb W. The flow rate in all cases was 50 ml/min of helium. The column temperature except where otherwise noted was 182°, and sample size 40 μ l, methyl ethyl ketone as solvent. The hydroquinone, deoxybenzoin, and benzil were all identified by trapping the respective peaks and comparing their infrared spectra with those of authentic samples. The quinone used was obtained by the method of MacCoy⁵. The benzoin was from Matheson, Coleman and Bell, m.p. 134–135°. The hydroquinone was B.D.H. Cert. m.p. 171–173°. Blank runs were made of both benzoin and quinone. In some cases to be absolutely sure the quinone was further purified by vacuum sublimation.

Results and discussion

As seen in Table I the amount of hydroquinone produced is almost linear with that of injected quinone but shows a slight tendency to level off which would be expected at a constant benzoin concentration. The general increase in the benzil/deoxybenzoin ratio would also be expected, the quinone would be competing with the benzoin for the

TABLE I
AMOUNTS OF PRODUCTS AFTER CHROMATOGRAPHY

Benzoin concn. M	Quinone concn. M	Quinone injected μ moles	Hydroquinone out μ moles	Benzil/deoxybenzoin
0.114	0.774	31.9	5.49	15.6
0.114	0.472	18.9	4.06	4.58
0.114	0.254	10.19	2.63	3.40
0.114	0.217	8.7	1.95	4.94
0.114	0.119	4.76	0.983	3.54
0.114	0.0	0.0	0.0	2.0

acceptance of the hydrogen. The lowest column temperature used was 158°, at which temperature at least 50 % as much hydroquinone is produced as at 182°.

Reactions occurring in the course of gas chromatography are well known, for example one can obtain catalytic isomerization of terpenes as well as catalytic and pure thermal decomposition of oxygenated terpenes^{1,2}. Dehydration, deacetylation, and *cis-trans* isomerization have all been observed in the GLC of the methyl esters of fatty acids³. These changes were primarily thermal but to some extent metal catalysed.

The reaction between benzoin and quinone is definitely thermal as it occurred on the simple heating of the two. On the other hand, the self reaction of benzoin is definitely catalysed by the column. The reaction between the benzoin and quinone is of interest as reactions involving hydrogen transfer during GLC are unusual and also GLC provides a convenient way to study this reaction⁴.

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¹ D. H. DESTY, *Gas Chromatography*, Academic Press, 1958, p. 214-215.

² E. A. DAY AND P. H. MILLER, *Anal. Chem.*, 34 (1962) 869.

³ L. J. MORRIS, R. T. HOLMAN AND KRISTER-FONTELL, *J. Lipid Res.* 1 (1959) 412.

⁴ S. Z. ROGINSKII, M. I. YANOVSKII AND G. A. GAZIEV, *Dokl. Akad. Nauk SSSR*, 140 (1961) 1125.

⁵ H. N. MACCOY, *J. Chem. Educ.*, 14 (1939) 494.

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