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POLYDENTATE PHOSPHONIUM SALTS FOR THE DEACTIVATION OF WALL-COATED OPEN-TUBULAR COLUMNS

COMPARISON OF TEMPERATURE STABILITY WITH OTHER DEACTIVATION METHODS

GEORGE MARCELIN, SEAN G. TRAYNOR, WILEY GOINS, Jr. and LINDA M. HIRSCHY
Organic Chemicals Division of SCM Corporation, P.O. Box 389, Jacksonville, Fla. 32201 (U.S.A.)
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SUMMARY

The deactivation of glass capillary columns by polydentate phosphonium bromides has been demonstrated and compared with other methods of deactivation in the temperature range of 150 to 325°. Glass capillary columns treated with tetradentate phosphonium bromides proved to be considerably more stable than columns treated with benzyltriphenylphosphonium chloride (BTPPCl), toasted Carbowax or silanizing agents. Columns deactivated with the polyphosphonium bromides and subsequently coated with a liquid phase showed excellent peak symmetry for highly polar compounds even after having been heated to 275° for 16 h. A column deactivated with BTPPCl and similarly coated showed a considerable loss of resolution when subjected to the same conditions.

INTRODUCTION

Glass capillary gas chromatography (GC) is rapidly becoming the preferred method for a wide variety of analytical problems. Compared with packed columns, capillaries offer higher efficiencies and lower pressure drops and therefore open the possibility for faster analysis using short columns[1,2].

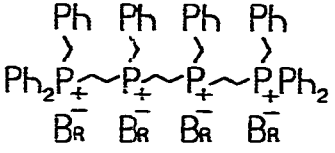
Glass is the preferred material for the manufacturing of capillary columns due to its chemical inertness and low cost. The surface of glass, however, shows great adsorption activity, particularly for polar compounds. This activity is manifested in the tailing of chromatographic peaks and the apparent loss of trace compounds during analysis; it is presumably due to the presence of free hydroxyl groups on the silica surface[3,4]. A variety of methods for deactivating the surface of glass are commonly used in preparing glass capillary columns: silanization[5,6], carbonizing[7], addition of surface active agents[8,9], formation of polymers[10,11], non-extractable films[12,13], and treatment with barium carbonate[14].

The analysis of heavy organic compounds or biological materials by glass capillary GC is a very complex and difficult task. Due to their low volatility, temperatures upwards of 300° are sometimes necessary to satisfactorily elute these compounds from a chromatographic column. The last decade has seen the number of high

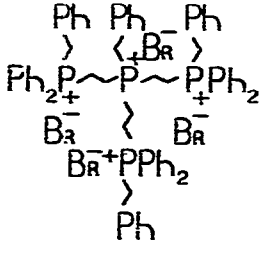
temperature GC phases increase rapidly, and there are presently phases available which are stable to over 350°[15,16]. Unfortunately, not much is known concerning the temperature stability of glass surfaces treated by various deactivation methods. Although several studies are available comparing the merits of various deactivation procedures[17,18], to our knowledge, there does not exist a thorough study of the effect of temperature on treated glass surfaces. We have observed, in our laboratory, that columns treated by any of the methods described above begin to exhibit peak-tailing after being heated to approximately 300° for extended periods of time.

The mechanism for deactivation of the glass wall by a surface active agent has been interpreted as involving the reaction of a surface silanol group with a deactivant[19]. At high temperatures these linkages can be broken and the surface active agent either eluted from the column or thermally degraded. Indeed, Malec[5] found that trioctadecylmethylammonium bromide decomposes at *ca.* 200° and columns deactivated by this agent show loss of resolution when heated above that temperature.

With the aim of preparing glass capillary columns which would be stable for long periods of time to temperatures in excess of 300°, we began looking at polyphosphonium salts analogous to benzyltriphenylphosphonium chloride (BTPPCl) as possible column deactivants. We reasoned that these salts could act as polydentate ligands on the glass surface and by virtue of their multiple points of attachment increased stabilization of the glass-deactivant linkages would occur. Additionally, because of their high molecular weight, they would not readily elute from the column at high temperatures. In this work we wish to report on the use of two novel compounds for the deactivation of glass capillary columns, 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane-1,4,7,10-tetrabenzyltetrabromide (PPBr-1) and tris(2-benzyldiphenylphosphoniumethyl)benzylphosphonium tetrabromide (PPBr-2), and their application for high temperature analysis.



(PPBr-1)



(PPBr-2)

The polyphosphonium compounds were compared with the more common methods of deactivation in terms of their ability to yield symmetric peaks from a glass capillary column which had been deactivated but not coated with a liquid phase. The effectiveness of the various deactivants against thermal degradation was investi-

gated by heating the columns to progressively higher temperatures and noting any loss of peak symmetry. Additionally, the temperature stabilities of some of the deactivants were compared using deactivated columns which had been conventionally coated with a liquid phase.

EXPERIMENTAL

Glass capillary columns were drawn on a Shimadzu GDM-1 glass-drawing machine using flint glass tubing which had been previously rinsed with acetone and dried. Columns with an I.D. of approximately 0.25 mm were cut to 20 m length and etched at 350° for 1 h with gaseous HCl as described by Franken *et al.*[20].

Following etching the columns were deactivated by one of the following methods: silanization, application of BTPPCl, heat treated Carbowax 20M, heat treated SP-2100 (Supelco, Bellefonte, Pa., U.S.A.) or application of one of the polydentate phosphonium bromides.

Silanization

Silanization was carried out by the method described by Novotný and Tesarik[5]. Dry nitrogen was bubbled through hexamethyldisilazane–trimethylchlorosilane (1:5) and passed through the column at room temperature for 1 h. The ends of the column were then sealed and the column heated to 200° for 48 h. The column was then opened and flushed thoroughly with nitrogen at room temperature.

BTPPCl

A plug of a 1–2% (w/w) solution of BTPPCl (Aldrich, Milwaukee, Wisc., U.S.A.) in dichloromethane was pushed through the column using dry nitrogen. The column was then washed with dichloromethane and dried with a stream of nitrogen.

Heat treated Carbowax 20M

The method described by Blomberg[13] was used for the preparation of a non-extractable layer of Carbowax 20M on a glass capillary. A slug of a 2–5% (w/w) solution of Carbowax 20M in dichloromethane was passed through the column at a rate of 10–20 mm/sec. The column was then flushed with dry nitrogen for several hours and the nitrogen-filled column sealed at both ends. The column was heated to 280° for 24–48 h and then thoroughly washed with 15 ml of dichloromethane and dried.

Heat-treated SP-2100

A method similar to the one described above for Carbowax 20M was used for the preparation of heat-treated SP-2100 columns. The major difference was the heat treatment temperature which in this case was 350°.

Application of polydentate phosphonium bromides

The polydentate phosphonium salts[21] PPBr-1 and PPBr-2 were dissolved in dimethylsulfoxide at a concentration of 1% (w/w) and approximately 3 ml of the solution were forced through the column. The column was then dried using a stream of nitrogen, sealed and heated to 200° for 3–5 h. At the end of this time period the

column ends were broken and the column flushed with 5–10 ml of dichloromethane followed by nitrogen flushing.

Procedure

After deactivation by the methods outlined above, the columns were connected to a Hewlett-Packard 5750 gas chromatograph which had been modified to operate with glass capillary columns. The column ends were connected to the splitter and the detector by means of graphite ferrules. A split of approximately 150:1 was used and the make-up gas flow was 30 ml/min. Helium was used exclusively as the carrier gas. All columns were operated isothermally at 150° and flow velocity was adjusted, by measuring an "unretained" peak (*i.e.*, hexane), to 20 cm/sec.

The procedure for measuring the thermal stability of the deactivation treatment consisted of connecting the column to the gas chromatograph and raising the temperature to the desired test temperature. After heating for a chosen length of time (usually 3 h) the temperature was brought down to 150° and a series of six compounds, each representing a different functional group, was injected. The tailing factor, as described by Schieke and Pretorius[17] was used as a measurement of the effectiveness of deactivation. The tailing factor is defined as

$$TF = a/b \times 100$$

where a and b are the half width of the front and rear portion of the peak at one-tenth the height, respectively.

The test compounds used were: (a) *n*-decane, a hydrocarbon; (b) 1-hexanol, an alcohol; (c) 5-nonanone, a ketone; (d) 2,5-dimethylaniline, a basic amine; (e) salicylaldehyde, a highly polar aromatic aldehyde; (f) linalyl acetate, a labile ester.

Several wall-coated open-tubular columns were fabricated using one of these deactivation methods in order to demonstrate the utility of the polydentate salts in a "real" analysis. These columns were deactivated with either BTPPCl or PPBr-1 and dynamically coated using a 15% solution of SP-2100 dissolved in dichloromethane using the mercury plug technique described by Schomburg and Husmann[22].

RESULTS AND DISCUSSION

The experiments conducted on glass capillary columns which had been deactivated but not coated show that the degree of tailing exhibited by a column depends, as expected, on the method of deactivation employed, the treatment temperature and the chemical nature of the compound used in determining the tailing factor. Fig. 1a–f shows the dependence of peak symmetry (*i.e.*, tailing factor) on treatment temperature and deactivation procedure for the six test compounds at temperatures ranging from 150 to 325.° In all cases heat treated SP-2100 proved to be the most ineffective deactivant, in most cases showing tailing factors less than 10 or no peaks at all. For this reason its results are not included in Fig. 1.

As chemical intuition would lead us to believe, it is relatively easy to deactivate columns for the analysis of hydrocarbons and other non-polar compounds. Fig. 1a shows that all methods of deactivation perform well at temperatures below 225°, with the phosphonium compounds (including BTPPCl) performing marginally better. As the temperature is increased however, we begin to see a breakdown on the peak symmetry of *n*-decane eluted from all columns. The temperature at which symmetry

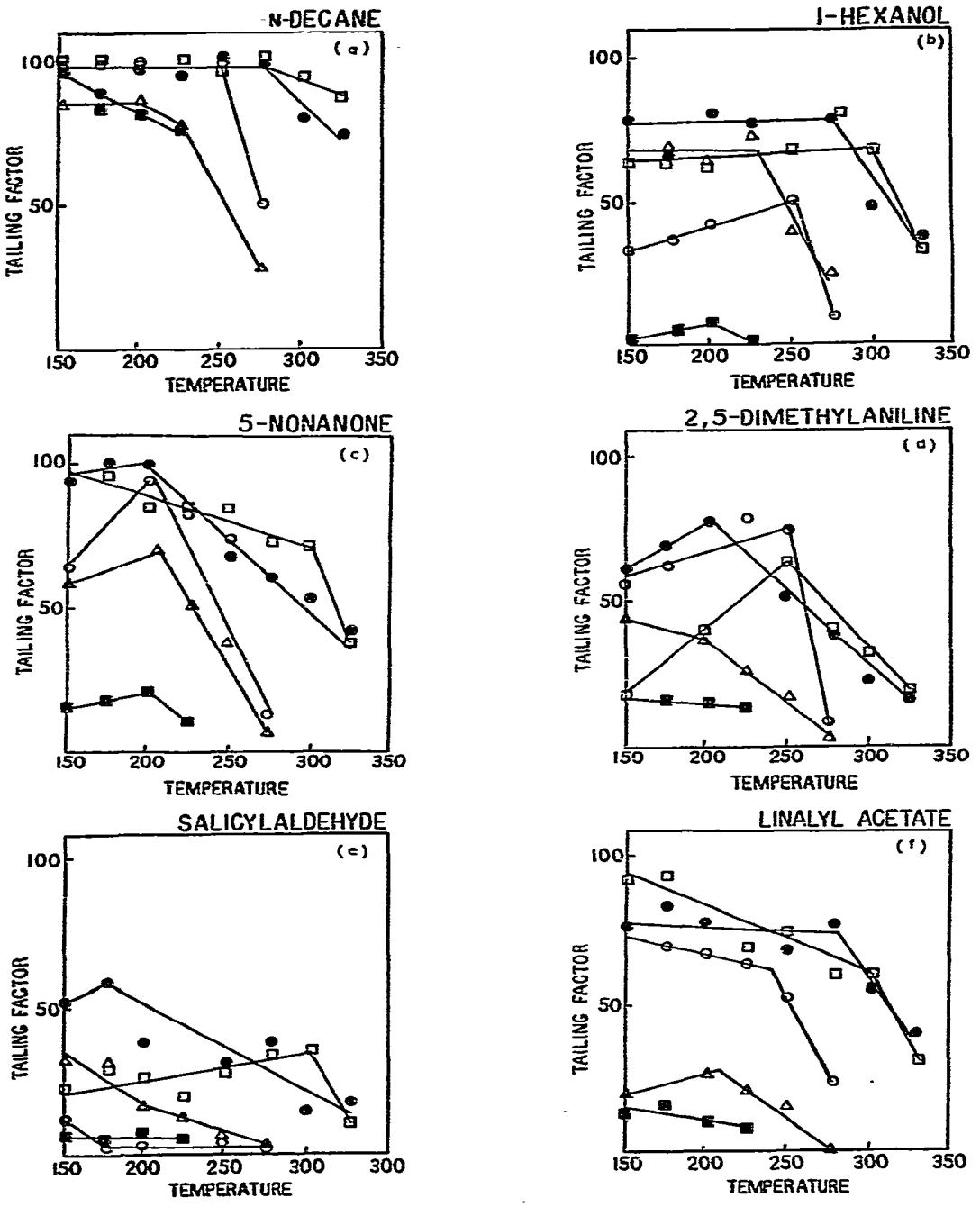


Fig. 1. Typical temperature dependence of tailing factors on glass capillary columns deactivated using various procedures. Test compounds used for the calculation of the tailing factors were: (a) *n*-decane; (b) 1-hexanol; (c) 5-nonanone; (d) 2,5-dimethylaniline; (e) salicylaldehyde; (f) linalyl acetate. Lines are estimated and drawn for reference only. ■, silanized; ○, BTPPCl; ●, PPBr-2; □, PPBr-1; △, Carbowax 20M.

breakdown occurs is different for each of the deactivation methods and is greatest for the polydentate phosphonium bromides, followed by BTPPCl, heat treated Carbowax 20M and silanizing, in that order.

The behavior of the other test compounds (Fig. 1b–f) parallel the results observed with *n*-decane, but here the difference becomes more obvious. In all cases we find that compounds eluting from columns deactivated with one of the tetradentate phosphonium salts retain higher peak symmetry to higher temperatures and again silanizing provides the poorest deactivation. It is interesting to note the behavior of 2,5-dimethylaniline on the phosphonium salts (Fig. 1d). We reproducibly found that maximum deactivation occurred after the column was heated to approximately 250°, perhaps indicating that a certain optimum temperature must be reached before coverage of all active sites is attained. After this work was completed we modified the deactivation procedure by increasing the initial temperature to which the column was heated from 200 to 250° (see Experimental section) in order to fully deactivate sites prior to coating with a liquid phase and although we have not explicitly investigated the effect of this temperature change on column performance we have observed no anomalous results.

In order to ascertain that the apparent higher temperature stability of the polydentate salts was in fact due to better deactivation and not to some surface phenomenon which would disappear when coated with a GC phase, two columns were deactivated with BTPPCl and PPBr-1, respectively and then coated with SP-2100. After heating the columns for a period of 16 h at 275° a solution containing 1-hexanol, *n*-decane, 5-nonanone and 2,5-dimethylaniline was analyzed in each column and the tailing factors for the individual components calculated. The averages of duplicate experiments are shown in Table I and, as expected, the column deactivated with PPBr-1 showed markedly better peak symmetry. It should be noted that prior to heating to 275° the column deactivated with BTPPCl had been conditioned to 225° and showed good peak symmetry. A more complex mixture containing as major components the *cis* and *trans* aldehydes, neral and geranial, along with other minor components was also examined in the SP-2100 columns which had been heated to 275°. These chromatograms are shown in Fig. 2 and demonstrate the severe tailing and loss of trace components that can occur when using a column which, although properly deactivated initially, has been heated to temperatures at which the deactivator breaks down.

The analogous bidentate and tridentate phosphonium bromides were also evaluated for their effectiveness to properly deactivate the glass surface. These two

TABLE I

COMPARISON OF COLUMNS TREATED WITH BTPPCl AND PPBr-1

Test compound	*Tailing factor*	
	BTPPCl	*PPBr-1*
1-Hexanol	13	66
n-Decane	96	97
5-Nonanone	28	89
2,5-Dimethylaniline	67	88

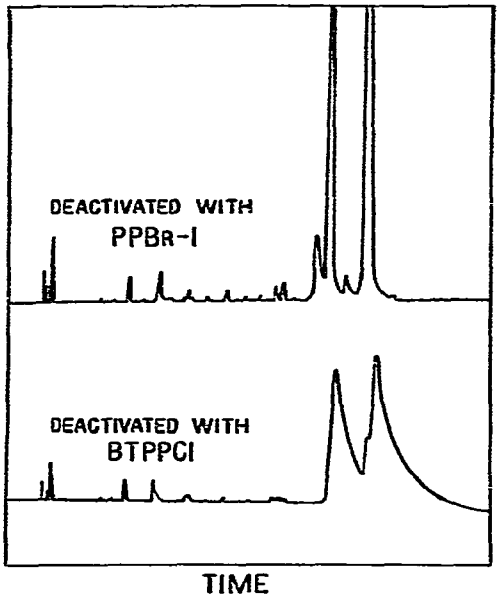


Fig. 2. Gas chromatographic trace of complex mixture analyzed on columns deactivated with PPBr-1 and BTPPCl, after the columns had been heated to 275° for 16 h. Fixed phase: SP-2100; initial temperature 75° programmed at 4°/min.

compounds proved to be good deactivants but their temperature stability was only marginally better than BTPPCl.

Much work remains to be done in the characterization of the polyphosphonium bromides and their utility as surface deactivants. We do not know if deactivation of borosilicate glass is possible with the polydentate salts, although we have no reason to believe the contrary. Now that these compounds are being made available* we hope other investigators will study them in more detail.

CONCLUSIONS

The severe tailing normally observed in glass capillary columns which have been taken to elevated temperatures can, in some cases, be attributed to breakdown of the deactivant–surface linkages. Polydentate phosphonium salts have been shown to increase the upper temperature limit of the inertness of capillary columns and improve the effectiveness of high-temperature liquid phases for GC analysis.

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* These compounds are now available through PCR Research, P.O. Box 1778, Gainesville, Fla. 32602, U.S.A.

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