

SEPARATION OF HEXENES BY GAS CHROMATOGRAPHY  
ON STATIONARY PHASES WITH PdCl<sub>2</sub>M. KRAJČIČ<sup>a</sup>, R. KOMERS<sup>b</sup> and F. ČŮTA<sup>c</sup><sup>a</sup> Pedagogical Institute, 306 19 Plzeň,<sup>b</sup> Institute of Chemical Process Fundamentals,

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The separation of the mixture of eight isomer hexenes and 2-methylpentane has been investigated on the PdCl<sub>2</sub>-N-methylacetamide solutions. The concentrations of 10% and 25% of PdCl<sub>2</sub> and a temperature of 30°C have been found as optimum separation conditions. With the exception of 1-hexene and *cis*-2-hexene all components of the mixture are separated on these stationary phases. On the contrary, the selectivity of the separation is worse with the reference phases (AgNO<sub>3</sub>-N-methylacetamide, N-methylacetamide, AgNO<sub>3</sub>-ethylene glycol and β,β'-oxydipropionitrile) under the comparable conditions. For the successful utilization of the stationary phases containing PdCl<sub>2</sub> and for the extension of the useful life of the column the necessary conditions considering the treatment have to be fulfilled, especially the elimination of water.

The procedures based on forming the π-complexes of the silver ion possess an important position among the analytical methods for the separation of the unsaturated compounds. These complexes are most frequently applied in the gas chromatography of alkenes. Since 1955, when Bradford, Harvey and Chalkley<sup>1</sup> reported their fundamental work, many papers (see<sup>2</sup>) have appeared in the literature. The successful utilization of forming the π-complexes of thallium<sup>3</sup> and rhodium<sup>4</sup> was described. The attempts of a gas chromatographic separation of the unsaturated compounds on the stationary phases containing compounds of other metals turned out to be more or less unsuccessful (see the survey<sup>5</sup>). Many of these attempts were focused on the use of the complexes of the unsaturated compounds with the metals of the platinum group. Studying the topic in question, first of all we have drawn our attention to the possibility of using the formation of monoalkene-PdCl<sub>2</sub> π-complexes for the separation. In the previous paper<sup>6</sup> an attempt was made to evaluate quantitatively the interactions of hexenes with the PdCl<sub>2</sub>-N-methylacetamide (NMA) solutions and the reference AgNO<sub>3</sub>-NMA solutions using some thermodynamic quantities calculated from the retention data. We have also investigated<sup>7</sup> the complex-forming reactions of hexenes in the PdCl<sub>2</sub>-NMA<sub>3</sub> systems, especially the complex stability of the individual hexenes and its relation to the structure, and finally the connection between the stability of complexes and the selectivity of these stationary phases.

The present paper deals with the possibility of utilizing the PdCl<sub>2</sub>-N-methylacetamide stationary phases for analytical purposes. For the comparative separation of hexenes the following liquid phases were used: AgNO<sub>3</sub>-NMA, AgNO<sub>3</sub>-ethylene glycol (EG), pure NMA and β,β'-oxydipropionitrile.

## EXPERIMENTAL

**Apparatus.** The apparatus used for the present study was the same as previously described<sup>8</sup>. For measuring the retention data a catharometer and a column of  $85 \times 0.4$  cm I.D. glass U-tube were employed. For the actual analysis a flame ionisation detector and a column of  $340 \times 0.6$  cm I.D. stainless steel U-tube were used. The samples were introduced as vapors by a syringe. The amounts of the individual hydrocarbons were approximately  $10^{-4}$  g, both for the pure hydrocarbons and for the mixtures prepared by their mixing.

**Materials.** In addition to the materials given in the previous paper<sup>6</sup> the following chemicals were used: ethylene glycol, purified by vacuum distillation of the reagent grade product, and Chromaton N—AW (0.20–0.25 mm) as the support of the stationary phase (both products were supplied by Lachema, Brno);  $\beta, \beta'$ -oxydipropionitrile (K and K Laboratories Inc., Plainview, N.Y., USA). Nitrogen was employed as the carrier gas at a flow rate of 30 to 60 ml/min.

**Preparation of the stationary phases and the column packing.** The preparation of the stationary phases consisting either of  $\text{PdCl}_2$ -NMA or  $\text{AgNO}_3$ -NMA and the coating of the support have already been described elsewhere<sup>6</sup>. Longer swirling was necessary for preparing solutions with more than 20% of  $\text{PdCl}_2$ . An equivalent procedure was also chosen for  $\text{AgNO}_3$ -EG. The stationary phases prepared in this way contained 5–28% of  $\text{PdCl}_2$  or 9.6% of  $\text{AgNO}_3$  in NMA and 24% of  $\text{AgNO}_3$  in EG. The packings were prepared by dissolving the stationary phase ( $\text{PdCl}_2$ -NMA,  $\text{AgNO}_3$ -NMA, NMA and  $\beta, \beta'$ -oxydipropionitrile) in dried acetone and slurrying them in the amount of 15 to 20% w/w with the support. The packed columns were conditioned for 12–100 hours at 30°C with the carrier gas flow.

**Retention data.** The retention data of the investigated hydrocarbons were expressed relative to *trans*-4-methyl-2-pentene as the standard. For this compound the specific retention volumes were calculated<sup>9</sup>.

## RESULTS AND DISCUSSION

The specific retention volumes of eight isomer hexenes and 2-methylpentane investigated at 30°C were determined for the total solubility region of  $\text{PdCl}_2$  in NMA (Fig. 1). Their numerical values are given in Table I for the selected concentrations of 10 and 25% of  $\text{PdCl}_2$  at which the selectivity of separation of the given mixture was found to be of the highest value. These data are listed together with the retention volumes of the individual hydrocarbons measured on the reference stationary phase of approximately the same molarity, i.e. 9.6 and 24% of  $\text{AgNO}_3$  respectively in NMA and EG. The retention volumes of *cis*- and *trans*-2-hexenes and 2-ethyl-1-butene at 30°C on all stationary phases used are given in Table II. The data obtained on the saturated solution of  $\text{AgNO}_3$  in EG (at 25°C) (ref.<sup>10</sup>) and the 0.05 mol/l solution of dicarbonyl-rhodium(I)-3-trifluoroacetyl-camphorate<sup>4</sup> (at 50°C) are listed for comparison.

We have stated in the previous papers<sup>6,7</sup> that the conditions for the sufficiently rapid reversible formation of the alkene- $\text{PdCl}_2$   $\pi$ -complexes were satisfied for the sorption of alkenes on the  $\text{PdCl}_2$ -NMA stationary phases in the gas chromatographic procedure. The differences in the structure between the  $\pi$ -complexes of hexe-

TABLE I  
Retention Volumes of Hexenes and 2-Methylpentane at 30°C

Compound	Boiling point <sup>15</sup> °C	Relative retentions					ODP <sup>a</sup>
		NMA <sup>a</sup>	PdCl <sub>2</sub> -NMA <sup>a</sup> (10% PdCl <sub>2</sub> )	PdCl <sub>2</sub> -NMA (25% PdCl <sub>2</sub> )	AgNO <sub>3</sub> -NMA (9.6% AgNO <sub>3</sub> )	AgNO <sub>3</sub> -EG <sup>a</sup> (24% AgNO <sub>3</sub> )	
2-Methylpentane	60.3	0.71	0.58	0.39	0.63	0.16	0.53
4-Methyl-1-pentene	53.9	0.92	1.43	2.02	1.10	2.45	0.95
<i>cis</i> -4-Methyl-2-pentene	56.3	0.96	1.70	2.93	1.17	2.82	1.06
<i>trans</i> -4-Methyl-2-pentene	58.6	1.00	1.00	1.00	1.00	1.00	1.00
2-Methyl-1-pentene	60.7	1.28	1.09	0.78	1.45	2.66	1.46
1-Hexene	63.5	1.29	2.29	3.62	1.70	4.40	1.35
2-Ethyl-1-butene	64.7	1.42	1.22	0.85	1.77	4.53	1.63
<i>trans</i> -2-Hexene	67.9	1.44	1.53	1.65	1.41	1.27	1.46
<i>cis</i> -2-Hexene	68.8	1.58	2.34	3.60	1.89	4.10	1.77
<i>V<sub>g</sub></i> ( <i>trans</i> -4-methyl-2-pentene), ml		78.7	68.4	61.3	66.2	9.9 <sup>b</sup>	13.9 <sup>b</sup>

<sup>a</sup> NMA N-methylacetamide, EG ethylene glycol, ODP  $\beta,\beta'$ -oxydipropionitrile; <sup>b</sup> *V<sub>g</sub>* were calculated from the measurements obtained by the F.I.D. supposing that the outlet pressure was equal to the barometric pressure.

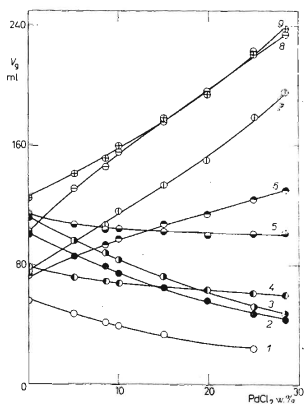


FIG. 1

Plots of the Specific Retention Volumes of Hexenes and 2-Methylpentane vs the Concentration of PdCl<sub>2</sub> in NMA at 30°C

1 2-Methylpentane; 2 2-methyl-1-pentene; 3 2-ethyl-1-butene; 4 *trans*-4-methyl-2-pentene; 5 *trans*-2-hexene; 6 4-methyl-1-pentene; 7 *cis*-4-methyl-2-pentene; 8 1-hexene; 9 *cis*-2-hexene.

TABLE II  
Retention Volumes of Hexenes at 30°C

Stationary phase	Relative retentions <sup>a</sup>			$V_g$ <i>trans</i> - -4-methyl- -2-pentene ml
	2-ethyl- -1-butene	<i>trans</i> - -2-hexene	<i>cis</i> - -2-hexene	
$\beta,\beta'$ -Oxydipropionitrile	1.63	1.46	1.77	13.9
NMA	1.42	1.44	1.58	78.7
$\text{PdCl}_2$ -NMA (10% $\text{PdCl}_2$ )	1.22	1.53	2.34	68.4
$\text{AgNO}_3$ -NMA (9.6% $\text{AgNO}_3$ )	1.77	1.41	1.89	66.2
$\text{PdCl}_2$ -NMA (25% $\text{PdCl}_2$ )	0.85	1.65	3.60	61.3
$\text{AgNO}_3$ -EG (24% $\text{AgNO}_3$ )	4.53	1.27	4.10	9.9
EG saturated by $\text{AgNO}_3$ <sup>10,b</sup>	4.77	1.34	4.86	—
Dicarbonyl-rhodium(I) -3-trifluoroacetylcamphorate (0.05 molal solution in squalane) <sup>4,c</sup>	0.65	1.77	3.49	—
Boiling point <sup>15</sup> , °C	64.7	67.9	68.8	

<sup>a</sup> Related to *trans*-4-methyl-2-pentene. <sup>b</sup> At 25°C. <sup>c</sup> At 50°C.

ne- $\text{PdCl}_2$  and  $\text{Ag}^+$  were expressed in the wider range of the stability constants of the hexene- $\text{PdCl}_2$   $\pi$ -complexes and the different value of the contribution of the complex-forming reaction to the total sorption interaction of the double bond. Therefore, the  $\text{PdCl}_2$ -NMA phases possess a higher selectivity for the separation of hexenes than  $\text{AgNO}_3$ -NMA (Table I). This advantage becomes more apparent in comparison with pure NMA and with  $\beta,\beta'$ -oxydipropionitrile.

In comparison with the pure solvent the presence of  $\text{PdCl}_2$  dissolved in NMA leads not only to the significant changes of the eluted hexenes order but also to the general increase of the selectivity because the separation ratio values increase in most cases. The retention ratios of *cis*-2-hexene related to 2-methyl-pentane were found 2.22, 4.05 and even 9.25, respectively, on pure NMA, on the 10% solution of  $\text{PdCl}_2$  in NMA and on the 25% solution of  $\text{PdCl}_2$  in NMA. Nevertheless, pure NMA possesses its own selectivity which contributes significantly to the separation and may improve the separation of the hydrocarbons. On the other hand the relatively high affinity of NMA to the hydrocarbons causes the simultaneous elution of the elkenes with alkanes possessing a higher number of carbon atoms (*e.g.* hexenes interfere with heptanes as is evident from the plots of the  $\log V_g$  vs boiling points of hydrocarbons)<sup>6</sup>.

The connection between the  $\text{PdCl}_2$  concentration and the separation selectivity is shown in Fig. 1 for 30°C. The concentration of about 10 and 25% of  $\text{PdCl}_2$  was found to be the most convenient for the separation of the mixture consisting of nine

investigated hydrocarbons because the differences among the relative retentions were the largest whereas the interference of eluted hexenes was suppressed to the minimum. As is evident from Fig. 1, the plot of the  $\log V_g$  vs concentration of  $\text{PdCl}_2$  in NMA show the increasing inclination with such hydrocarbons where higher values of the stability<sup>7</sup> constants of the originating  $\pi$ -complexes were found and where the salting out effect of dissolved  $\text{PdCl}_2$  plays an important role. On the contrary, the hydrocarbons forming the complexes of low stability are indicated by a decreasing plot of the  $\log V_g$  vs the  $\text{PdCl}_2$  concentration because the salting out effect plays an important role compared with that of the complex forming reaction.

Because the melting point of NMA is 27°C and the usable temperature range is limited to 20–40°C, the temperature of 30°C was chosen for the comparison separation on the different columns. A temperature of 30°C was found to be the most convenient for the separation of the investigated mixture of hexenes on 10%  $\text{PdCl}_2$

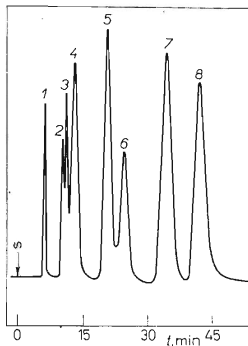


FIG. 2

Separation of Hexenes and 2-Methylpentane on a 25% Solution of  $\text{PdCl}_2$  in NMA at 30°C

Column 340 × 0.6 cm; 15% of the stationary phase on Chromaton N-AW (0.20–0.25 mm),  $\text{N}_2$  35 ml/min. 1 2-Methylpentane; 2 2-methyl-1-pentene; 3 2-ethyl-1-butene; 4 *trans*-4-methyl-2-pentene; 5 *trans*-2-hexene; 6 4-methyl-1-pentene; 7 *cis*-4-methyl-2-pentene; 8 1-hexene, *cis*-2-hexene.

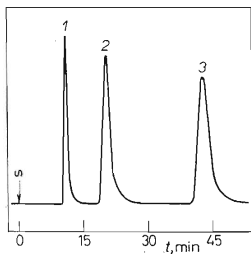


FIG. 3

Separation of Some Hexenes on a 25% Solution of  $\text{PdCl}_2$  in NMA at 30°C

Column 340 × 0.6 cm; 15% of the stationary phase on Chromaton N-AW (0.20–0.25 mm);  $\text{N}_2$  35 ml/min. 1 2-Ethyl-1-butene; 2 *trans*-2-hexene; 3 *cis*-2-hexene.

in NMA, as is obvious from the plot of the  $\log V_g$  vs  $1/T$  (ref.<sup>6</sup>). With the stationary phase containing 9.6%  $\text{AgNO}_3$  in NMA the optimum selectivity was found at approximately 20°C. The effect of temperature on the selectivity is considerably lower in this case than with the corresponding  $\text{PdCl}_2$ -NMA phases. A small range of usable temperature also limits the utilization of these stationary phases for the separation of  $\text{C}_4$ - $\text{C}_7$  hydrocarbons and it is very likely the best for the hydrocarbons of  $\text{C}_5$ - $\text{C}_6$ .

The comparison of the separation of the investigated mixture on the phases in question at 30°C does not correspond to the strictly optimum experimental conditions on the individual columns. It is evident from the partial measurements of the HETP vs  $u$  that the experimental conditions chosen for the individual columns were close to the optimum values. Considering that practically all these conditions used for the comparison were identical or very similar to one another (*e.g.* the support, the geometry of the column, *etc.*), the separation differences can be explained by the selective properties of the individual stationary phases, particularly with  $\text{PdCl}_2$ -NMA and  $\text{AgNO}_3$ -NMA.

Because of the high selectivity of the solutions of  $\text{PdCl}_2$  (10 and 25%), the separation of eight isomer hexenes and 2-methylpentane is much better than that achieved on the  $\text{AgNO}_3$  solutions in NMA or EG of the same molarity and also on any other phase compared, as can be seen from the chromatograms. The efficiency of the columns containing  $\text{PdCl}_2$ -NMA phases expressed by the height equivalent to a theoretical plate is comparable or even better than that attained with the different solutions of  $\text{AgNO}_3$  (refs<sup>11-13</sup>). It is approximately 0.15 and 0.25 cm respectively for 10 and 25% of  $\text{PdCl}_2$ . According to the literature<sup>4</sup> not even the stationary phases with rhodium compounds achieve the HETP value lower than 0.1 cm.

If the  $\text{PdCl}_2$ -NMA stationary phases are used it is necessary to avoid such conditions which are favourable for the reactions deteriorating the column packing and cutting its useful life. This fact was mentioned in the previous paper<sup>7</sup>. In addition to the possibility of forming the  $\pi$ -allyl complexes between the alkenes and  $\text{PdCl}_2$  above 50°C, the presence of water represents a main danger for the strongly hygroscopic stationary phase. Also in very small amount water decomposes the alkene-metal  $\pi$ -complexes; this reaction can lead to both the formation of some aldehydes and palladium metal and also to undesirable isomeric reactions. In order to employ the method successfully the following conditions must be fulfilled: the elimination of the air humidity, perfect drying of the carrier gas, and sufficient conditioning of the column packing. The fact that the stationary phases containing  $\text{AgNO}_3$  are noted for limited stability<sup>14</sup> and gradual breakdown is also valid for the  $\text{PdCl}_2$ -NMA solutions. The elimination of both daylight and high temperature is a necessary condition in preparing these solutions and in handling the packing of the column. In spite of the careful handling the columns with the 20% solutions of  $\text{PdCl}_2$  did not survive more than one week as far as unimportant changes of the retention data were concerned. On the contrary, the columns with 10% solution of  $\text{PdCl}_2$  were some-

times used one month without any important deterioration. Moreover, with the phase containing 20% of PdCl<sub>2</sub> difficulties arising from its slower solubility, and worse reproducibility of the retention data was observed.

In spite of the same difficulties which are connected with handling the stationary phases in question the method described can be considered convenient for investigating the sorption processes. Unfortunately, utilization for the analytical separation of isomer alkenes (Figs 2 and 3) seems to be less promising.

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