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GAS CHROMATOGRAPHIC DETERMINATION OF THE TEMPERATURE LIMIT OF ALKYLPYRIDINE–TRISODIUM PHOSPHATE COMPLEX FORMATION AND ITS USE IN IDENTIFICATION

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SUMMARY

The specific retention volumes, partial molar free energies, enthalpies and entropies of sorption have been determined for eleven pyridine bases on two columns with hydrogenated Apiezon L containing equimolar quantities of trisodium phosphate or potassium fluoride. Thermodynamic characteristics of complex formation between alkylpyridines and trisodium phosphate have been calculated. The determination of the temperature limit for such complex formation by gas chromatography has been elaborated. A method of identification of alkylpyridines in mixtures with hydrocarbons is proposed. The procedure involves comparison of the retention indices of the compounds on the column containing Apiezon L and trisodium phosphate at two analysis temperatures. Alkylpyridines are characterized by sharply decreasing retention indices with increasing temperature.

INTRODUCTION

The presence of trisodium phosphate and potassium fluoride in packed and capillary columns containing polar PEG-40M or non-polar hydrogenated Apiezon L does not influence the retention indices of hydrocarbons[1,2]. Unlike hydrocarbons, organic bases are capable of forming donor–acceptor complexes with these salts[3,4]. The differences in the ability of these salts to undergo donor–acceptor interactions with organic bases under gas chromatographic (GC) conditions have been estimated thermodynamically[1]. It has been demonstrated that alkylpyridines form complexes with trisodium phosphate but not with potassium fluoride[3,4].

Earlier, the temperature stability of donor–acceptor complexes formed by organic bases with alkali was studied under GC conditions[5]. It was proposed to make use of the ability of primary and secondary amines to form hydrogen-bonds with sodium hydroxide for their identification according to the temperature coefficient of the retention indices[5,6].

In the present work the thermodynamic stability of alkylpyridine–trisodium phosphate complexes under GC conditions was studied and the possibility of using this type of complexing in the analysis of alkylpyridines in mixtures with hydrocarbons was demonstrated.

EXPERIMENTAL

Pyridine and ten alkylpyridine derivatives (Table I) were subjected to chromatography on two glass columns (270 × 0.4 cm I.D.) containing equimolar quantities of potassium fluoride or trisodium phosphate (0.004 mol of each) and 4% hydrogenated Apiezon L on Chromosorb G AW (100–120 mesh). The molecular weight of the hydrogenated Apiezon L determined ebullioscopically was 2400. The columns were prepared as described[1]. The separation of aromatic hydrocarbons, benzene, toluene, o- and p-xylenes, was carried out only on the column containing trisodium phosphate. The boiling points of the analyzed compounds were in accord with the literature data. The retention of alkylpyridines was determined at 80, 100, 120 and 130°C, the retention of aromatic hydrocarbons at 80 and 130°C. Analyses carried out on a Pye-Unicam 104 chromatograph with a flame ionization detector. The carrier gas (helium) flow-rate was 30–40 ml/min. The compounds were analyzed as solutions in pentane. The sample (1 µl) contained 5–10 µg of each compound.

Retention indices, I, specific retention volumes, V_g, and thermodynamic parameters of sorption of alkylpyridines were determined. Hydrocarbons were characterized by the retention indices.

For determination of V_g, the formula[7]

$$V_g = \frac{273 t' V}{TW} \cdot j \left(1 - \frac{P_{H_2O}}{P_o} \right)$$

was used where t' is the corrected retention time in min, V is the bulk flow-rate (ml/min) of the carrier gas measured at room temperature with a foam flow-rate meter, W is the mass (g) of stationary phase in the column, T is room temperature (K), $1 - P_{H_2O}/P_o$ is a correction for the water vapour pressure at room temperature and j is a factor taking into account the pressure drop in the column

$$j = \frac{3}{2} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}$$

where P_i is the inlet pressure and P_o is the outlet pressure.

The partial molar free energies of sorption were determined by the equation[7]

$$\Delta G = -RT\ln \frac{V_g M}{273 R'}$$

where M is the molecular weight of the hydrogenated Apiezon L, T is the analysis temperature (K), R, R' is the gas constant equal to 1.987 cal/mol · K, 82.0577 ml · atm/mol · K. The enthalpies and entropies of sorption were determined by the known equations:

$$\Delta H = -R \frac{d \ln V_g}{d\, 1/T}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

RESULTS AND DISCUSSION

For the study of the interaction of alkylpyridines with trisodium phosphate, the compounds listed in Table I were analyzed on a column of hydrogenated Apiezon L (4%) and trisodium phosphate. As a reference we used a column containing an equal quantity of stationary phase and equimolar potassium fluoride instead of trisodium phosphate. Potassium fluoride does not form complexes with tertiary amines under GC conditions[8]. Both columns had practically identical sorption properties as regards substances incapable of specific interaction with salts, e.g., n-octane (see Table I). The differences in column properties are manifested in the analysis of alkylpyridines which can behave as electron donors. For this reason, the retention of these compounds is greater in the presence of trisodium phosphate in comparison to potassium fluoride. Thus, the partial molar free energy, enthalpy and entropy of donor–acceptor complexing can be described by the following relationships:

$$\Delta G_{\text{d-acc}} = \delta(\Delta G)_{\text{Na}_3\text{PO}_4,\ \text{KF}} = \Delta G_{\text{Na}_3\text{PO}_4} - \Delta G_{\text{KF}}$$
$$\Delta H_{\text{d-acc}} = \delta(\Delta H)_{\text{Na}_3\text{PO}_4,\ \text{KF}} = \Delta H_{\text{Na}_3\text{PO}_4} - \Delta H_{\text{KF}} \tag{1}$$
$$\Delta S_{\text{d-acc}} = \delta(\Delta S)_{\text{Na}_3\text{PO}_4,\ \text{KF}} = \Delta S_{\text{Na}_3\text{PO}_4} - \Delta S_{\text{KF}}$$

The results of calculations of $\Delta G_{\text{d-acc}}$, $\Delta H_{\text{d-acc}}$ and $\Delta S_{\text{d-acc}}$ are given in Table II. The contribution of the free energy of the donor–acceptor interaction of alkylpyridines with trisodium phosphate, $\delta(\Delta G)_{\text{Na}_3\text{PO}_4,\ \text{KF}}$, to the total sorption energy is 3–12% at 100°C, depending on the substance. At the same time, the contributions of the enthalpy, $\Delta H_{\text{d-acc}}$, and entropy, $\Delta S_{\text{d-acc}}$, to the total thermodynamic sorption values are considerable and may be as high as 40 and 60%, respectively.

TABLE I

SPECIFIC RETENTION VOLUMES, V_g (ml/g), AND PARTIAL MOLAR FREE ENERGIES OF SORPTION, ΔG(cal/mol), OF ALKYLPYRIDINES

Columns with hydrogenated Apiezon L and trisodium phosphate or potassium fluoride at 100 and 120°C.

Compound	Trisodium phosphate				Potassium fluoride			
	100°C		120°C		100°C		120°C	
	V_g	$-\Delta G$	V_g	$-\Delta G$	V_g	$-\Delta G$	V_g	$-\Delta G$
Pyridine	48.0	1214	34.3	1016	36.8	1017	31.0	937
2-Methylpyridine	78.0	1574	52.4	1347	63.6	1422	50.6	1320
3-Methylpyridine	116.6	1871	73.7	1614	87.1	1655	67.2	1541
4-Methylpyridine	118.2	1882	75.3	1630	90.6	1684	69.1	1563
2,6-Dimethylpyridine	113.3	1850	76.8	1646	98.5	1746	74.2	1619
2,5-Dimethylpyridine	190.2	2234	112.3	1942	151.9	2067	109.4	1922
2,3-Dimethylpyridine	201.9	2278	127.7	2043	163.4	2122	118.9	1987
3-Ethylpyridine	216.8	2331	130.2	2058	173.7	2167	125.4	2029
2-Propylpyridine	247.8	2430	159.1	2215	217.3	2333	152.2	2180
4-Propylpyridine	444.0	2862	244.4	2550	348.8	2684	233.2	2514
2-Butylpyridine	505.6	2959	294.4	2695	446.8	2867	291.0	2685
n-Octane	53.5	1291	40.2	1140	54.0	1301	40.4	1144

TABLE II

COMPARISON OF THE THERMODYNAMIC CHARACTERISTICS OF SORPTION OF ALKYL-PYRIDINES ON THE HYDROGENATED APIEZON L COLUMNS WITH TRISODIUM PHOS-PHATE OR POTASSIUM FLUORIDE

Compound	$-\delta(\Delta G)_{Na_3PO_4, KF}$ at 100°C (cal/mol)	$-\delta(\Delta G)_{Na_3PO_4, KF}$ at 120°C (cal/mol)	$-\Delta H_{Na_3PO_4}$ at 100–120°C (kcal/mol)
(1) Pyridine	193	79	4.91
(2) 2-Methylpyridine	152	27	5.81
(3) 3-Methylpyridine	216	73	6.69
(4) 4-Methylpyridine	198	67	6.59
(5) 2,6-Methylpyridine	104	27	5.68
(6) 2,5-Dimethylpyridine	167	20	7.70
(7) 2,3-Dimethylpyridine	156	56	6.69
(8) 3-Ethylpyridine	164	29	7.45
(9) 2-Propylpyridine	97	35	6.47
(10) 4-Propylpyridine	178	36	8.72
(11) 2-Butylpyridine	92	10	7.90

If the same mechanism of complexing with trisodium phosphate applies to all the studied alkylpyridines, there should be an isokinetic relationship between the enthalpies and entropies of complex formation for this group of compounds[9,10]. In our case, such a relationship really does exist for the studied organic bases (see Fig. 1), i.e.:

$$\Delta H_{d\text{-acc}} = k \cdot \Delta S_{d\text{-acc}} \tag{2}$$

The correlation coefficient for our linear relationship is 0.9992. The existence of the isokinetic relationship for all the alkylpyridines under test shows that the same type of complex is formed in each case. Complex formation, as shown earlier[4], probably takes place due to the following interaction: $O = \overset{|}{P}- \cdots \overset{|}{N}-$. It is worth mentioning that the isokinetic relationship is realized only for $\Delta H_{d\text{-acc}}$ and $\Delta S_{d\text{-acc}}$ values; general thermodynamic characteristics of sorption of the same compound, $\Delta H_{Na_3PO_4}$ and $\Delta S_{Na_3PO_4}$, are not described by eqn. 2, as can be calculated from data in Table II.

The values of $\delta(\Delta G)_{Na_3PO_4, KF}$ at 120°C are lower than those at 100°C (see Table II). The contribution of complex formation to the total free energy of sorption reduces to zero at the temperature limit, T_{lim}:

$$\Delta G_{d\text{-acc}} = \Delta H_{d\text{-acc}} - T_{lim} \cdot \Delta S_{d\text{-acc}} = 0 \tag{3}$$

This temperature limit is easily calculated by the ratio:

$$T_{lim} = \frac{\Delta H_{d\text{-acc}}}{\Delta S_{d\text{-acc}}} = \frac{\delta(\Delta H)_{Na_3PO_4, KF}}{\delta(\Delta S)_{Na_3PO_4, KF}} \tag{4}$$

$-\Delta H_{KF}$ at 100–120°C (kcal/mol)	$-\delta(\Delta H)_{Na_3PO_4, KF}$ at 100–120°C (kcal/mol)	$-\Delta S_{Na_3PO_4}$ at 100°C (cal/K · mol)	$-\Delta S_{KF}$ at 100°C (cal/K · mol)	$-\delta(\Delta S)_{Na_3PO_4, KF}$ at 100°C (cal/K · mol)
2.51	2.40	9.91	3.99	5.92
3.54	2.47	11.36	5.15	6.21
3.79	2.90	12.92	5.70	7.22
3.96	2.63	12.62	6.10	6.52
4.14	1.54	10.27	6.42	3.85
4.80	2.90	14.65	7.31	7.34
4.64	2.05	11.84	6.76	5.08
4.71	3.74	13.72	6.82	6.90
5.20	1.27	10.84	7.69	3.15
5.88	2.84	15.71	8.57	7.14
6.26	1.64	13.26	9.11	4.15

Values of T_{lim} calculated from the data in Table II are given in Table III: they lie between 122 and 132°C. GC analysis of alkylpyridines at a temperature above T_{lim} has verified our approach. For example, at 150°C, the retention indices of alkylpyridines on the column with Apiezon L and trisodium phosphate and are the same as those on the reference column with Apiezon L and potassium fluoride.

On the basis of the data obtained it is possible to propose a method of identification of alkylpyridines in mixtures with other compounds that do not interact with trisodium phosphate. The method consists in the comparison of the retention parameters of the studied compounds at two temperatures —close to T_{lim} and below
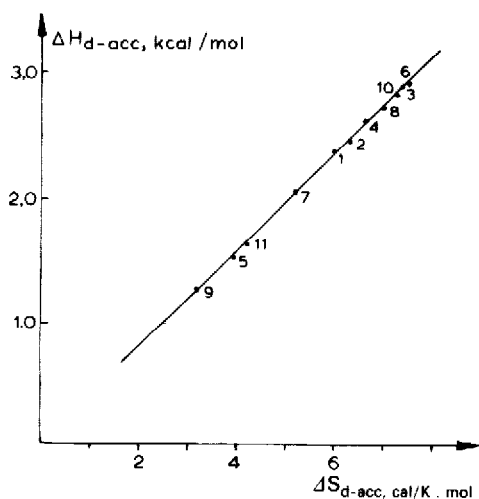

Fig. 1. Relationship between the enthalpies and the entropies of donor–acceptor interaction between alkylpyridines and trisodium phosphate under GC conditions. The compounds are numbered as in Table II.

TABLE III

TEMPERATURE LIMIT, T_{lim}, OF ALKYLPYRIDINE–TRISODIUM PHOSPHATE COMPLEX FORMATION UNDER GC CONDITIONS

Complex with	$T_{lim}(°C)$	Complex with	$T_{lim}(°C)$
Pyridine	132	2,3-Dimethylpyridine	130
2-Methylpyridine	125	3-Ethylpyridine	124
3-Methylpyridine	129	2-Propylpyridine	130
4-Methylpyridine	130	4-Propylpyridine	125
2,6-Dimethylpyridine	127	2-Butylpyridine	122
2,5-Dimethylpyridine	122		

TABLE IV

RETENTION INDICES OF ALKYLPYRIDINES AND AROMATIC HYDROCARBONS ON COLUMN CONTAINING HYDROGENATED APIEZON L AND TRISODIUM PHOSPHATE AT 80 AND 130°C

Compound	I_{80}	I_{130}	∂I
Pyridine	808	758	−50
2-Methylpyridine	871	832	−61
4-Methylpyridine	932	886	−46
3-Ethylpyridine	1011	973	−38
Benzene	680	688	8
Toluene	788	797	9
p-Xylene	891	901	10
o-Xylene	915	929	14

it— on the same column containing a non-polar stationary phase and trisodium phosphate. As an example, Table IV gives retention indices of four alkylpyridines and four aromatic hydrocarbons at 80 and 130°C. For pyridines, the retention indices sharply decrease (by approximately 50 i.u. per 50°C increase in the analysis temperature), while the retention indices of hydrocarbons increase slightly (by 8–14 i.u. in the same temperature interval). Thus, the changes in alkylpyridine retention indices depending on the analysis temperature are significant and can be used to identify these organic bases in mixtures with hydrocarbons.

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