Temperature changes of sorption parameters of di-*n*-alkylketones and methylcyclohexanones in capillary gas chromatography

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The gas chromatographic behavior of di-*n*-alkylketones and isomeric methylcyclohexanones at variable temperatures in the isothermal runs has been studied using three capillary columns coated with SE-30, OV-225, and PEG-40M/KF stationary phases. The retention indices and their temperature increments were determined, and the partial molar free energies of the compounds under study were calculated. A linear dependence of the values of the partial molar free energy of sorption on the homologue number in di-*n*-alkylketones is not observed for the first member on the nonpolar SE-30 phase and for the third member on the polar OV-225 and PEG-40M/KF phases.

Key words: capillary gas chromatography, di-*n*-alkylketones, methylcyclohexanones; retention indices, temperature increments; partial molar free energy of sorption.

Previously,[1] a reduced sorption ability has been demonstrated by the GLC technique for the first and third members of the homologous series of organic compounds where the growing *n*-alkyl radical is directly bonded to the carbonyl group. The assumption was made that in the case of the first homologue the weakening of its interaction with the stationary phase is due to a weak van der Waals interaction of the adjacently bonded methyl and carbonyl groups. Previously,[1,2] a thermodynamic estimate of the abnormal GLC behavior of the first homologue in the series of methyl-*n*-alkylketones, butyl-*n*-alkylketones, phenyl-*n*-alkylketones, and methyl esters and chloroanhydrides of saturated acids has been made. The decrease in the energy of sorption of the third homologue is due likely to the capability of the Pr-substituent to form conformers with plausible intramolecular interactions of the terminal Me group with the electron pair of the carbonyl group.[3]

It was of interest to elucidate whether the "propyl effect" exists in di-*n*-alkylketones, to estimate the effect of the polar phases, capable of donor-acceptor interactions, on the thermodynamic characteristics of the first and the third members of the series and to compare the thermodynamic characteristics of symmetric ketones and those of positional isomers of methylcyclohexanone, for which the intramolecular interaction of the carbonyl group and the Me substituent is impossible because of their characteristic conformational features.

The aim of the present work is to determine the partial molar free energies of sorption and the retention indices of aliphatic and cyclic ketones, to elucidate the influence of the polarity of the stationary phase on the sorption characteristics of the homologues of di-*n*-alkylketones and methylsubstituted cyclohexanones, and to determine the temperature increments of indices used as one of the criteria of identification of the substances.

Experimental

The retention indices and the partial molar free energies of sorption for homologues in the series of di-*n*-alkylketones $(R_m)_2C=O$ (m = 1—4), methylalkylketones $R_mC(O)Me$ (m = 1—4), and positional isomers of methylcyclohexanone were determined. GLC analysis was performed on a Micromat-412 (Finland) instrument with a flame ionization detector. Two used silica capillary columns (25 m×0.32 mm) coated with SE-30 (a film 1.0 μm thick) and PEG-40M/KF (a film 0.2 μm thick) stationary phases and a glass capillary column (50 m×0.30 mm) coated with OV-225 (a film 0.2 μm thick) stationary phase were used. The columns with PEG-40M/KF and OV-225 were prepared following the known procedures.[4,5] Helium was used as the carrier gas, and isothermal analyses were carried out at 80, 90, 100, and 110 °C. The inlet pressure was 0.7, 0.5, and 1.0 atm for columns with SE-30, PEG-40M/KF, and OV-225, respectively. The inlet split ratio of the flow was 1 : 100. The sample volume of a 0.2% acetone solution of the mixture of chromatographically pure isomers of methylcyclohexanone was 0.2 μL. Mixtures of di-*n*-alkylketones and methylalkylketones were prepared from equal volumes of pure substances, and the vapors (0.1 μL) were injected into the column.

The reference *n*-alkanes C_6—C_{14} were analyzed before and after the compounds investigated. The volumes of samples of 0.2% pentane solutions of *n*-alkanes were 0.1 μL. The hold-up time of the chromatographic system was determined from the retention time of methane injected simultaneously with the compounds analyzed. The retention indices were calculated by the Kováts formula[6] using the experimental values of corrected retention times as an average over 5—7 runs. Standard devia-

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Table 1. The retention indices of methylcyclohexanones, di-*n*-alkylketones, and methyl-*n*-alkylketones on capillary columns of different polarities at temperatures of analysis between 80 and 110 °C

Compound	SE-30				OV-225				PEG-40M/KF			
	80	90	100	110	80	90	100	110	80	90	100	110
R-Cyclohexanone												
R = H	874	877	881	883	1235	1245	1255	1267	1278	1288	1297	1304
CH_3 (2)	929	932	935	937	1259	1268	1278	1289	1292	1302	1310	1317
CH_3 (3)	931	934	937	939	1280	1290	1301	1312	1310	1321	1330	1337
CH_3 (4)	936	939	943	945	1288	1299	1309	1321	1320	1330	1339	1347
R—C(O)—R												
R = CH_3	477	478	481	484	762	761	759	755	809	806	802	798
C_2H_5	682	682	682	681	949	952	953	954	978	980	980	980
C_3H_7	859	859	859	860	1110	1114	1116	1119	1123	1126	1128	1129
C_4H_9	1060	1060	1059	1059	1311	1315	1319	1322	1316	1320	1324	1325
CH_3—C(O)—R												
R = CH_3	477	478	481	484								
C_2H_5	582	583	585	587								
C_3H_7	672	673	674	676								
C_4H_9	774	774	775	777								

Note. Reproducibility of the values of I is ±2 iu on polar columns.

tions of the values of the retention indices did not exceed ±2. The values of the partial molar free energies of sorption were calculated using the formula:

$$\Delta G = -2.3\ RT\log(k'\beta), \qquad (1)$$

where R = 8.3143 J mol^{-1} grad^{-1} is the universal gas constant; T/K is the temperature of analysis; $k' = (t - t_m)/t_m$ is the capacity factor, t is the retention time of the substance, t_m is the hold-up time of the non-sorbed gas (methane); $\beta = (d_c - 2d_f)^2/4d_f(d_c - d_f)$ is the phase ratio, d_c is the inner diameter of the column, d_f is the film thickness of the stationary phase. The standard deviations of ΔG values calculated using formula (1) did not exceed ±0.050 kJ mol^{-1}.

Results and Discussion

The effect of temperature of the GC analysis and the polarity of the stationary phase on the sorption characteristics of ketones was studied on the three capillary columns at 80, 90, 100, and 110 °C. The substances under study were characterized by their values of the capacity factors (k'), the retention indices (I), temperature increments of indices ($10 \cdot \delta I/\delta T$), as well as by the values of the partial molar free energy of sorption (ΔG) at the indicated temperatures of the analysis. As can be seen from Table 1 and 2, the values of indices of methylcyclohexanones increase with increasing temperature and polarity of the column. All positional isomers of methylcyclohexanone are well resolved only on the polar OV-225 and PEG-40M/KF stationary phases. Their temperature increments of the retention indices on the polar phases are very large for ketones (see Table 2).

The retention indices of isomeric methylcyclohexanones increase on all three stationary phases as the distance between the methyl substituent and the $\gt$C=O group increases. The most pronounced increase in the indices was observed on the OV-225 and PEG-40M/KF phases. It is apparently associated with increasing the orientative interaction between 3- and 4-methylcyclohexanones compared with that of the 2-methyl-substituted isomer. However, in contrast to heterocycles containing the Me substituent in the α-position to the heteroatom, there is no sharp decrease in the retention of the 2-methyl-substituted cyclohexanone as compared to other isomers, *i.e.*, the "α-effect" [7] is absent. This can be explained by the absence of the van der Waals interaction between the $\gt$C=O group and the substituent in α-position because of the chair conformation of

Table 2. Temperature increments of the retention indices ($10 \cdot \delta I/\delta T$) of methylcyclohexanones, di-*n*-alkylketones, and methyl-*n*-alkylketones on capillary columns of different polarities

Compound	SE-30	OV-225	PEG-40M/KF
R-Cyclohexanone			
R = H	3.0	11.0	9.0
CH_3 (2)	3.0	10.0	8.0
CH_3 (3)	3.0	11.0	9.0
CH_3 (4)	3.0	10.0	9.0
R—C(O)—R			
R = CH_3	2.0	−2.0	−4.0
C_2H_5	—	2.0	1.0
C_3H_7	—	3.0	2.0
C_4H_9	—	4.0	3.0
CH_3—C(O)—R			
R = CH_3	2.0		
C_2H_5	1.7		
C_3H_7	1.0		
C_4H_9	1.0		

the cycle. This is also evidenced by the nearly equal temperature increments for all positional isomers of methylcyclohexanone (see Table 2). The temperature increments of positional isomers of methylcyclohexanone on polar OV-225 and PEG-40M/KF phases can be used as identification markers in analyzing their mixtures with aliphatic ketones.

In the series of dialkylketones the character of a change in the retention indices with increasing temperature of analysis is the same for symmetric and asymmetric ketones; in this case the temperature increments are small (with allowance for experimental error). The only exception is the first member of the series, acetone, for which an insignificant increase in the index on SE-30 column and a decrease in the index with increasing temperature on the polar phases are observed. The temperature increment is negative on the polar OV-225 and PEG-40M columns only for acetone.

A thermodynamic estimate of the gas chromatographic behavior of positional isomers of methylcyclohexanone and symmetric di-*n*-alkylketones was made using the values of the partial molar free energy of sorption (ΔG) on the three stationary phases under study. The values of ΔG of the studied compounds calculated by formula (*1*) are presented in Table 3. The values of ΔG_{exp} for methyl-*n*-alkylketones on a nonpolar column with SE-30 are also given therein for comparison. As can be seen from Table 3, the ΔG values are little changed in the temperature interval studied and depend on the polarity of the column.

The experimental values of ΔG_{exp} for the homologues of di-*n*-alkylketones were compared with the calculated values of ΔG_{calc} obtained from a linear dependence $\Delta G = f(m)$, where m is the homologue number ($m = 1$—4). As can be seen from Fig. 1, departures from the linear dependence were observed on the nonpolar SE-30 phase for the first and third members of the homologous series (acetone and dipropylketone, respectively) in the case of methylketones (0.2—0.1 kJ mol^{-1}), and for the first member of the homologous series in the case of symmetric ketones (0.6 kJ mol^{-1}). Small deviations (0.3—0.4 kJ mol^{-1}) were observed on the polar columns with OV-225 and PEG-40M/KF only for dipropylketone; in the series of symmetric ketones the first member of the series obeys (within the limits of experimental errors) a linear dependence on the homologue number (Table 4).

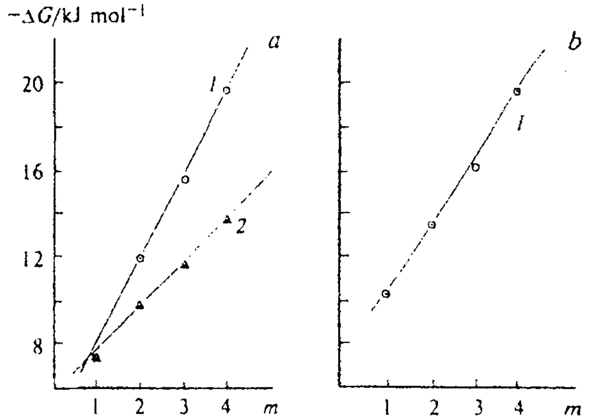
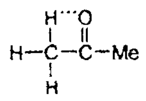


Fig. 1. Dependence of the partial molar free energy of sorption (ΔG) on the homologue number (m) on capillary columns of different polarities at 100 °C: *a*, column with SE-30; *b*, column with PEG-40M/KF (*1*, di-*n*-alkylketones; *2*, methyl-*n*-alkylketones).

The previously found[1] decrease in the retention of the first member of the homologous series of methyl-*n*-alkylketones, acetone, is likely associated with an intramolecular van der Waals interaction (*1*).



$$\mathrm{H{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H\cdots}{|}}{C}}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Me}$$

(*1*)

Therefore, and in the series of di-*n*-alkylketones, where the first member is also acetone, its departure from the linear dependence $\Delta G = f(m)$ is observed on a column with SE-30.

Table 3. Dependences of the partial molar free energies of sorption ($-\Delta G$/kJ mol^{-1}) on the temperature of analysis (80—110 °C) for methylcyclohexanones, and symmetric and asymmetric alkylketones on capillary columns of different polarities

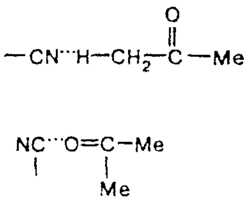
Compound	SE-30				OV-225				PEG-40M/KF			
	80	90	100	110	80	90	100	110	80	90	100	110
Cyclic ketones												
Cyclohexanone	17.05	16.54	16.06	15.55	20.45	19.86	19.19	18.68	20.24	19.70	19.11	18.72
2-Methylcyclohexanone	18.22	17.68	17.17	16.63	20.92	20.31	19.60	19.07	20.51	19.96	19.35	18.95
3-Methylcyclohexanone	18.26	17.73	17.21	16.66	21.34	20.73	20.02	19.49	20.85	20.30	19.70	19.30
4-Methylcyclohexanone	18.38	17.84	17.33	16.78	21.50	20.88	20.17	19.64	21.03	20.48	19.88	19.48
Symmetric ketones												
Acetone	8.16	7.76	7.46	7.16	10.98	10.54	10.03	9.68	11.15	10.67	10.32	9.83
Diethylketone	12.88	12.42	11.99	11.51	14.79	14.25	13.64	13.20	14.45	13.97	13.51	13.09
Dipropylketone	16.73	16.16	15.64	15.09	17.98	17.35	16.65	16.10	17.25	16.69	16.15	15.91
Dibutylketone	21.00	20.32	19.68	19.03	21.92	21.18	20.36	19.70	20.96	20.30	19.66	19.13
Methyl-*n*-alkylketones												
Acetone	8.16	7.76	7.48	7.19								
Methylethylketone	10.57	10.14	9.77	9.43								
Methylpropylketone	12.59	12.11	11.69	11.30								
Methylbutylketone	14.81	14.28	13.80	13.35								

Table 4. The differences ($\delta(\Delta G)$/kJ mol^{-1}) between the experimental values of the partial molar free energies of sorption (ΔG_{exp}, see Table 3) and those calculated from the linear dependence (ΔG_{calc}), for di-*n*-alkylketones and methyl-*n*-alkylketones on capillary columns of different polarities at temperatures of analyses 80 and 100 °C

Compound	*m**	SE-30			OV-225			PEG-40		
		ΔG_{calc}		$-\delta(\Delta G)$	ΔG_{calc}		$-\delta(\Delta G)$	ΔG_{calc}		$-\delta(\Delta G)$
		80	100	80, 100	80	100	80, 100	80	100	80, 100
Symmetric ketones										
Acetone	1	8.75	8.08	0.6	11.05	10.10	0.1	11.16	10.35	0
Diethylketone	2	12.81	11.93	−0.1	14.70	13.53	−0.1	14.43	13.46	0
Dipropylketone	3	16.87	15.77	0.1	18.32	16.96	0.3	17.70	16.57	0.4
Dibutylketone	4	20.93	19.62	−0.1	21.96	20.40	0	20.97	19.68	0
Methyl-*n*-alkylketones										
Acetone	1	8.42	7.73	0.3**						
Methylethylketone	2	10.54	9.74	0						
Methylpropylketone	3	12.66	11.75	0.1						
Methylbutylketone	4	14.78	13.77	0						

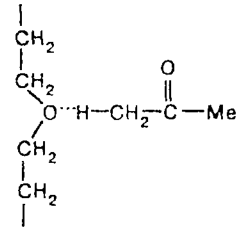
* *m* is the homologue number. ** At 100 °C $-\delta(\Delta G)$ = 0.2 kJ mol^{-1}.

On the polar OV-225 and PEG-40M/KF phases, the intramolecular interaction (*1*) seemingly does not occur because of a feasible competing intermolecular interaction with the fragments of the stationary phase.



(*2*)

for OV-225



(*3*)

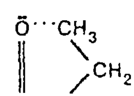
for PEG-40M/KF

This makes possible to indirectly estimate the order of magnitude of the interaction of the intramolecular fragment (*1*) and the stationary nonpolar phase, for instance, by the use of data obtained on a column with SE-30 at 100 °C. The energy of such interaction is defined as the difference between the value of ΔG_{exp} (−7.48 kJ mol^{-1}) and that of ΔG_{calc} (−7.73 kJ mol^{-1}) calculated for acetone from the linear dependence $\Delta G = f(m)$ for the series of methylketones (m = 1−4):

$$\delta(\Delta G)_{MeC(O)Me} = \Delta G_{calc} - \Delta G_{exp} = -0.25 \text{ kJ mol}^{-1}.$$

The change of the positive sign of the temperature increment of acetone on the column with SE-30 to the negative one for columns with OV-225 and PEG-40M, while the sign of the temperature increments of the rest of the homologues of the series on these phases is positive, can serve as confirmation of the change of the van der Waals interaction from type (*1*) to (*2*) and (*3*) (see Table 2). This fact shows the change in the character of the van der Waals interaction of the first homologue as compared to the other members of the series.

Another picture was observed in the case of the third member of the homologous series, dipropylketone. Whereas the difference between ΔG_{calc} and ΔG_{exp} is only −0.14 kJ mol^{-1} on the polar column with SE-30 at 80 °C, the departure from the linear dependence $\Delta G = f(m)$ on the polar OV-225 and PEG-40M/KF stationary phases amounts to −0.34 and −0.45 kJ mol^{-1}, respectively (Table 4). The "propyl anomaly" expressed as a decrease in the energy of the interaction between the third member of the homologous series and the stationary phase was first found[8,9] for homologous series of substances containing a π-electron system in the molecule. The authors of Refs. 8, 9 explained this phenomenon by an intramolecular donor-acceptor interaction of the propyl substituent with the π-electron system of the molecule. In our case, it might be the van der Waals interaction (*4*), which is energetically more favorable than interactions (*1*) and (*2*).



(*4*)

It seems plausible that in the case of formation of such a structure the molecule becomes more compact, and the energy of its interaction with the stationary phases decreases. Except the methyl and propyl homologues, good coincidence between the experimental and the calculated values of the partial molar free energies of sorption is observed for the other members of the series.

The results obtained show that studying the temperature changes in the sorption parameters and their thermodynamic estimate allows one to reveal fine effects of the van der Waals interaction between *n*-aliphatic and cyclic ketones with stationary phases of different polarity.

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