Temperature dependence of the Kovats retention indices for alkyl 1,3-diketones on a DB-5 capillary column

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Abstract: A series of alkyl 1,3-diketones were used to study the temperature dependence of the Kovats retention indices in the temperature range 130–190 ºC (403–463 K). The temperature dependence is described by the empirical equation $I = B + B/T + C\ln T$. On the basis of this equation, the activation enthalpy, $\Delta H^{\neq}$, and the chemical potential of the partitioning of one methylene group between the two phases of the chromatographic system, $\Delta u_{p(CH_2)}$, were calculated. Also, the Kovats retention indices – boiling point correlations (linear and reciprocal) for alkyl 1,3-diketones were studied and $\Delta u_{p(CH_2)}$ was calculated.

Key*words*: retention indices, alkyl 1,3-diketones, temperature dependence.

INTRODUCTION

Following James and Martin,[1] Kovats[2] elaborated a universal retention system. Since then different relationships have been used to describe the dependence of the Kovats retention indices on temperature. In most of the examples described in the literature, the dependence of the Kovats indices on the isothermal column temperature can be presented by a straight-line plot[3–5] as given by the linear Eqs. (1) and (2), which describe the dependence of the retention index on the column temperature t, ºC or $1/T$, K^{-1}:

$$I = a + bt \qquad (1)$$

$$I = A + B/T \qquad (2)$$

The most popular relationship describing the temperature dependence of the Kovats indices in non-linear systems is the Antoine type equation:[6,7]

$$I = A + \frac{B}{C + T} \qquad (3)$$

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For non-polar analytes chromatographed on non-polar stationary phases, the dependence of the retention index on temperature is almost linear.[6,7] On the other hand, for polar analytes chromatographed on non-polar stationary phases, the observed non-regularity can be well described by the equation:[8–10]

$$I = A + \frac{B}{T} + C \ln T \qquad (4)$$

where A, B and C are equation constants.

The final form of Eq. (4) can be achieved in two different ways, *i.e.*, by use of "kinetic" and "thermodynamic" models. The "thermodynamic" approach is based on the Kirchhof law and the "kinetic" model, proposed by Kowalska, is founded on kinetic concepts (transition state theory, theory of phase transfer, and the Eyring equation) as well as on thermodynamic premises.[8] The equation constants A, B and C have a physicochemical meaning and by using two of the constants it is possible to calculate the so-called activation enthalpy $\Delta H^{\neq}$ and the chemical potential of partitioning of one methylene group between the stationary and mobile phases, $\Delta \mu_{p(CH_2)}$.[8]

A series of synthesized alkyl 1,3-diketones were used to determine the Kovats retention indices isothermally on a DB-5 capillary column in the temperature range 130–190 ºC (403–463 K). The observed non-linear dependence of the Kovats indices on temperature were analysed using Eq. (4) and the activation enthalpy, $\Delta H^{\neq}$, and the chemical potential of the partitioning of one methylene group between the two phases of the chromatographic system, $\Delta \mu_{p(CH_2)}$, were calculated. Also, the Kovats retention indices – boiling point correlations for the alkyl 1,3-diketones were studied and $\Delta \mu_{p(CH_2)}$ was calculated.

EXPERIMENTAL

The GC analyses were performed on a Varian 3400 gas chromatograph equipped with a flame ionization detector and an all-glass split-splitless sample injector (1071 capillary injector). Data handling was provided by a Varian 4720 data system.

The DB-5 capillary column (McReynolds polarity = 323) was obtained from J & W Scientific, Folsom, CA, USA, dimensions 60 m × 0.321 mm, film thickness 0.25 µm, theoretical plates/meter 3409 for tridecane, coating efficiency 94.5 for tridecane. The column was operated under isothermal conditions (130, 150, 170 and 190 ºC).

The carrier gas was nitrogen, carrier gas flow 1 ml/min, injector temperature 250 ºC, split ratio 1:60, detector temperature 300 ºC, attenuation 1 and range 10^{-10} A/mV.

The studied alkyl 1,3-diketones except acetylacetone were synthesized using the procedure given by Claisen and Erdhardt.[11,12] The purity of all products was controlled by GC, IR and ^{1}H-NMR.[12]

The hydrocarbons used in this study as standards were obtained from Fluka (Switzerland).

RESULTS AND DISCUSSION

The mean values of the Kovats retention indices from the three series of measurements of the alkyl 1,3-diketones on DB-5 capillary column in the temperature range 130–190 ºC (403–463 K) are given in Table I.

Table II contains numerical values of the constants from Eq. (4) (A, B and C), regression coefficient and numerical values of T_{max} (corresponding to the maximum on the plot

of I against T) predicted by use of Eq. (4). Table III gives the thermodynamic values of $\Delta H^{\neq}$ and $\Delta u_{p(CH2)}$ for each individual chromatographic system.

TABLE I. The Kovats retention indices of alkyl 1,3-diketones on a DB-5 capillary column in the temperature range 130–190 °C (403–463 K).

Alkyl 1,3-diketone	Compound No.	T/K				T_B^*/K
		403	423	443	463	
2,4-Pentanedione	1	786.6	787.25	763.43	691	411
2,4-Hexanedione	2	888.2	892.19	895.93	800	434
2,4-Heptanedione	3	977.42	982.81	983.82	891.08	449
5-Methyl-2,4-hexanedione	4	940.17	944.07	945.33	850.54	447
2,4-Octanedione	5	1079.34	1083.01	1086.32	991.42	463
6-Methyl-2,4-heptanedione	6	1028.7	1032.09	1033.26	936.02	470
5,5-Dimethyl-2,4-heptanedione	7	988.41	993.79			477
2,4-Nonanedione	8	1136.19	1217.13	1216.04	1119.04	497

* The T_B data are experimental and the calculated boiling points at atmospheric pressure were taken from Scifinder database-data calculated using Advanced Chemistry Developoment (ACD) Software Solaris V4.67.

TABLE II. Terms A, B and C of Eq. (4) (R – regression coefficient, number of points = 4, and the calculated temperature maximum (T_{max}))

Alkyl 1,3-diketone	$A \pm s_A$	$B \pm s_B$	$C \pm s_C$	R	T_{max}
2,4-Pentanedione	129540.70 ± 22928.40	−7618504.60 ± 1399996.30	−18311.78 ± 3243.66	0.9962	416
2,4-Hexanedione	170252.20 ± 80408.69	−10138725.79 ± 4909711.88	−24039.46 ± 11375.35	0.9527	421.7
2,4-Heptanedione	167628.99 ± 72835.75	−9975263.91 ± 4447312.08	−23654.85 ± 10304.01	0.9597	421.7
5-Methyl-2,4-hexanedione	168665.16 ± 75863.14	−10033219.21 ± 4632162.97	−23809.84 ± 10732.29	0.9584	421.4
2,4-Octanedione	168267.52 ± 79134.48	−10006133.52 ± 4831909.47	−23731.59 ± 11195.09	0.9535	421.6
6-Methyl-2,4-heptanedione	172134.35 ± 78053.27	−10232403.60 ± 4765891.32	−24291.01 ± 11042.13	0.9584	421.2
2,4-Nonanedione	296118.89 ± 22419.89	−1797661.63 ± 1368946.57	−41737.09 ± 3171.72	0.9971	430.7

From comparison of the Kovats retention indices obtained (Table I), it is obvious that the change of retention index in the temperature range 130–190 °C (403–463 K) can be well described using Eq. (4) and the observed maximum temperature is in the lower regions of the working temperature (Table II). Although for most of the alkyl 1,3-diketones T_{max} is around 421, generally there is an increase of T_{max} from 2,4-pentanedione to 2,4-nonanedione (Fig. 1).

TABLE III. The activation enthalpy, $\Delta H^{\neq}$, and the chemical potential of the partitioning of one methylene group between the two phases of the chromatographic system, $\Delta u_{p(CH_2)}$, of alkyl 1,3-diketones.

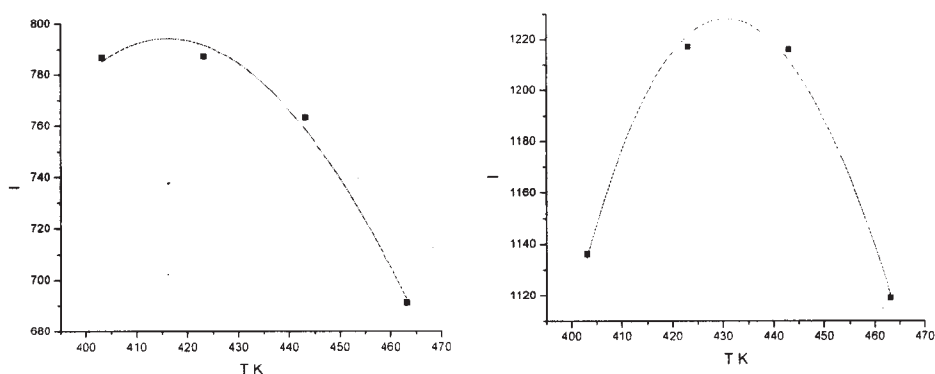| Alkyl 1,3-diketone	Number of carbon atoms	$\Delta H^{\neq}$	$\Delta u_{p(CH_2)}$
2,4-Pentanedione	5	–3458	19.66
2,4-Hexanedione	6	–3506	14.98
2,4-Heptanedione	7	–3506	15.22
5-Methyl-2,4-hexanedione	7	–3503	15.12
2,4-Octanedione	8	–3505	15.17
6-Methyl-2,4-heptanedione	8	–3502	14.82
2,4-Nonanedione	9	–3581	8.62

Fig. 1. Graphical presentation of the dependence of the Kovats retention indices on temperature for 2,4-pentanedione (a) and 2,4-nonanedione (b) on a DB-5 capillary column.

The numerical value of the temperature at the maximum on the *I-T* plot (Fig. 1) can be calculated by fitting terms *B* and *C* of Eq. (4):

$$T_{max} = \frac{B}{C} \tag{5}$$

where T_{max} is the temperature of the gas chromatographic analysis at which the numerical value of the retention index is highest for a given analyte, under the employed working conditions.

The same terms which enable the determination of T_{max} can also be used for calculation of the enthalpy of activation, $\Delta H^{\neq}$:[8]

$$B = \frac{100}{\ln K_{p(CH_2)}} \left(-\frac{\Delta H^{\neq}}{R} \right) \tag{6}$$

and

$$C = \frac{100}{\ln K_{p(CH_2)}} \tag{7}$$

where R is the universal gas constant, 8.314 J mol^{-1} K^{-1}, and $K_{p(CH_2)}$ is a constant for the partitioning of one methylene group between the two phases of the chromatographic system. After the required transformations, the following relationship is obtained:[8]

$$\Delta H^{\neq} = -\frac{B}{C} R = -T_{max} R$$

(8)

The range of magnitude of $\Delta H^{\neq}$ for alkyl 1,3-diketones can be compared with the energies of weak intermolecular interactions. The occurrence of any chemical reaction is excluded, because the energy involved would be at least an order of magnitude higher. This leads to a conclusion that the chromatographic process, which in the "kinetic" approach is depicted as a series of equilibria of the vaporization↔solution type,[8] is a purely physical process. The enthalpy of activation can be described as the heat of adsorbtion and/or desorption at the temperature T_{max}. Its negative sign suggests an exothermic process with the equilibrium shifted towards solution, whereas $\Delta H^{\neq}$ can be regarded as the heat of adsorption of the molecule on the surface of the stationary phase from the gas phase.

Considering the experimental values of $\Delta H^{\neq}$, it can be observed that $\Delta H^{\neq}$ increases with increasing carbon chain length. Branching in the alkyl 1,3-diketones decreases $\Delta H^{\neq}$. These tendencies are illustrated in Fig. 2.
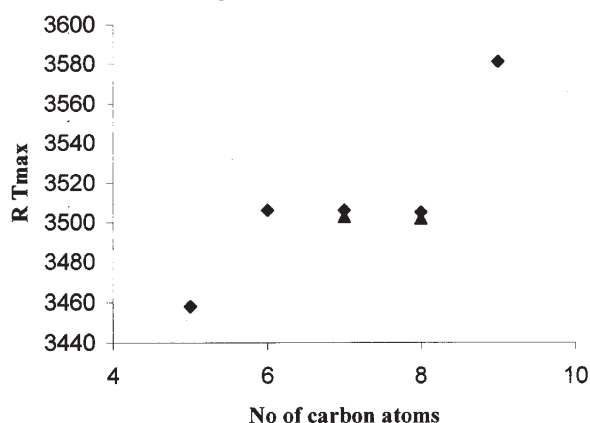

Fig. 2. Dependence of the activation enthalpy on the number of carbon atoms for linear (◆) and branched (▲) alkyl 1,3-diketones.

Another thermodynamic property which can be determined by use of Eq. (4) is the chemical potential of partitioning of one methylene group between the two phases of the chromatographic system, $\Delta\mu_{p(CH_2)}$. This can be obtained from term C of Eq. (7).[8] As:

$$\Delta\mu_{p(CH_2)} = -RT \ln K_{p(CH_2)},$$

(9)

it is apparent that:

$$\Delta\mu_{p(CH_2)} = -\frac{100R\overline{T}}{C}$$

(10)

where $\overline{T}$ is the mean temperature of the range of temperatures applied (433 K in this work).

Eq. (10) predicts very low value for $\Delta\mu_{p(CH_2)}$ (Table III), which are significantly lower than the values reported in the literature.[13] The value of $\Delta\mu_{p(CH_2)}$ can also be obtained using equations which correlate the retention index with the boiling points of an analyte:[13]

$$I = \left(\frac{100 \times 85}{\Delta\mu_{p(CH_2)}} \right) T_B - \frac{100 \times 85 \times T}{\Delta\mu_{p(CH_2)}} \tag{11}$$

or

$$I = a \times T_b + b \tag{12}$$

where $a = \dfrac{100 \times 85}{\Delta\mu_{p(CH_2)}}$ and $b = -\dfrac{100 \times 85 \times T}{\Delta\mu_{p(CH_2)}}$

Also, the reciprocal model can be used:[13]

$$I = \frac{100 \times \Delta\overline{H}_{vap}}{\Delta\mu_{p(CH_2)}} - \frac{100 \times \Delta\overline{H}_{vap} \times T}{\Delta\mu_{p(CH_2)}} \times \frac{1}{T_B} \tag{13}$$

or

$$I = \frac{c}{T_B} + d \tag{14}$$

where $c = -\dfrac{100 \times \Delta\overline{H}_{vap} \times T}{\Delta\mu_{p(CH_2)}}$ and $d = \dfrac{100 \times \Delta\overline{H}_{vap}}{\Delta\mu_{p(CH_2)}}$.

Eq. (13) can be rearranged using the corrected boiling point $(T_B - T)$ instead of T_B:[13]

$$I = \left(\frac{100 \times \Delta\overline{H}_{vap}}{\Delta\mu_{p(CH_2)}} \right) \times \left(1 - \frac{T}{T_B} \right) \tag{15}$$

or

$$I = b_0 + b_1 \left(1 - \frac{T}{T_B} \right) \tag{16}$$

where only b_1 has a physicochemical interpretation $b_1 = \dfrac{100 \times \Delta\overline{H}_{vap}}{\Delta\mu_{p(CH_2)}}$.

Statistical evaluation of the quality of the fits of the experimental values of I and the experimental and calculated T_B values to the linear and reciprocal models (Eqs. (12, 14, 16)) is given in Tables IV and V. Table IV summarizes the results of the fits by the linear

model in the form of Eq. (12). Table V summarizes the results of the fit by the reciprocal models in the form of Eq. (14), and of Eq. (16). The description of the linear model is slightly better than that of the reciprocal models.

TABLE IV. Kovats retention index *vs.* boiling point. Regression summary for the linear model $I = aT_B + b$ (Eq. 12) (R – regression coefficient, n – number of points, S – standard error)

	403	423	443	463
a, slope	4.00	4.66	4.92	4.70
b, intercept	−851.47	−1136.38	−1250.31	−1241.52
R	0.9860	0.9814	0.9881	0.9868
n	8	8	7	7
S	19.68	26.54	24.24	24.37

TABLE V. Kovats retention index *vs.* boiling point. Regression summary for the reciprocal models $I = c/T_B + d$ (Eq. 14) and $I = b_0 + b_1(1 - T/T_B)$ (Eq. 16) (R – regression coefficient, n – number of points, S – standard error)

	403	423	443	463
c, slope	−820586	−946197	−1005464	−957883
d, intercept	2781.76	3071.26	3205.26	3008.20
b_1, slope	2036	2236	2269	2068
b_0, intercept	745.56	834.39	935.59	939.38
R	0.9870	0.9740	0.9857	0.9821
n	8	8	7	7
S	18.98	26.54	26.57	28.38

TABLE VI. Comparison of the calculated $\Delta u_{p(CH_2)}$ values using Eqs. (11, 13, 15)

	$\Delta u_{p(CH_2)}$/J mol^{-1}						
T/K	From a, Eq. (11)	From b, Eq. (11)	From c,[*] Eq. (13)	From d,[*] Eq. (13)	From b_1,[*] Eq. (15)	Average value	Literature value
403	2125	4023	1493	2041	2041	2344	
423	1824	3163	1353	1858	1858	2011	1935[**]
443	1727	3012	1296	1831	1831	1939	2032[***]
463	1808	3171	1381	2008	2008	2075	

[*]$\Delta \overline{H}_{vap}$ value was obtained using ΔH_{vap} values taken from Scifinder database-data calculated using Advanced Chemistry Development (ACD) Software Solaris V4.67; [**]SE-52 (McReynolds polarity = 334), T = 383 K (Ref. 13); [***]OV-3 (McReynolds polarity = 423), T = 383 K (Ref. 13)

Table VI summarizes the results of a comparison for $\Delta u_{p(CH_2)}$ obtained using parameters a, b, c, d and b_1 according to Eqs. (11, 13, 15) and from the literature. The fairness of the results depends on the precision of the ΔH_{vap} value which was obtained using the ΔH_{vap} values taken from the Scifinder database for the investigated alkyl 1,3-diketones.

The $\Delta u_{\mathrm{p(CH_2)}}$ values obtained in such a manner resemble the literature data for similar stationary phases much better than the data obtained using the "kinetic" model.

CONCLUSION

The Kovats retention indices of alkyl 1,3-diketones were studied in the temperature range 130–190 ºC (403–463 K). The temperature dependence is described by the equation $I = A + B/T + C\ln T$. On the basis of this equation, the activation enthalpy, $\Delta H^{\neq}$, and the chemical potential of the partitioning of one methylene group between the two phases of the chromatographic system, $\Delta u_{\mathrm{p(CH_2)}}$, were calculated. The rather insignificant values of $\Delta H^{\neq}$ indicate that in the investigated chromatographic system, the occurring processes are exclusively physical (and not chemical). The negative values of $\Delta H^{\neq}$ indicate that the equilibrium of the vaporization$\leftrightarrow$solution process is shifted towards solution. Also, the Kovats retention indices – boiling point correlations for the alkyl 1,3-diketones were studied using linear and reciprocal models and $\Delta u_{\mathrm{p(CH_2)}}$ was calculated. The obtained value of $\Delta u_{\mathrm{p(CH_2)}}$ from these correlations is closer to literature data than the values obtained using the "kinetic" model.

ИЗВОД

ТЕМПЕРАТУРНА ЗАВИСНОСТ КОВАЧЕВИХ РЕТЕНЦИОНИХ ИНДЕКСА 1,3-ДИКЕТОНА НА DB-5 КАПИЛАРНОЈ КОЛОНИ

ДУШАН Ж. МИЈИН и ДУШАН Г. АНТОНОВИЋ

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У раду су дати Ковачеви ретенциони индекси 1,3-дикетона добијени на капиларној колони DB-5 у температурном интервалу 130–190 ºC. Добијени ретенциони индекси анализирани су коришћењем израза $I = A + B/T + C\ln T$. На основу добијених вредности константи B и C израчуната је вредност енталпије активације, $\Delta H^{\neq}$, као и партициони хемијски потенцијал, $\Delta u_{\mathrm{p(CH_2)}}$. Такође је разматрана зависност Ковачевог ретенционог индекса од температуре кључања 1,3-дикетона употребом линеарног и реципроционих модела. Из добијених вредности константи датих модела израчунат је партициони хемијски потенцијал, $\Delta u_{\mathrm{p(CH_2)}}$.

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