A SIMPLE METHOD FOR ESTIMATING VAPORIZATION PROPERTIES OF PHEROMONE-LIKE ACETATES FROM THEIR MOLECULAR STRUCTURES

Bohumír KOUTEK, Michal HOSKOVEC and Jan VRKOČ

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6

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A simple computational method has been developed to determine vapor pressures of pheromone-like acetates. The input parameters required, i.e. critical temperatures and critical pressures are obtained from the known molecular structures by using group contribution methods. Subsequently, the vapor pressures are estimated by the three parameter corresponding states equation of Lee and Kesler. The validity of this approach was tested on a homogeneous experimental material (eleven C_{10} to C_{16} acetates) by standard methods of statistical analysis, as well as by comparison of the results with corresponding experimental data. When compared with GC based experimental values, the estimated vapor pressures show mean relative error $< \pm 10\%$, achieving thus a better accuracy than other experimental methods when compared among themselves. A close correlation, viz. $\ln t_{1/2} = -0{\cdot}294 \ln P + 1{\cdot}82$ ($r = 0{\cdot}9986$) has been found between first order half-lives for evaporative loss of acetates from rubber septa and calculated vapor pressures.

Over the past two decades there has been a massive increase in the amount of research aimed at studying the chemistry of pheromones as well as possible applications these pheromones might have in the control of insect populations[1-3]. Chemical studies of sex pheromones have shown that, with few exceptions, females release a blend of several chemical components in a specific ratio and release rate[4,5]. Hence, to mimic a pheromone-releasing insect in practical applications, it became necessary to develop controlled release systems for use in monitoring, mass trapping, and aerial dissemination control programs. It is generally supposed[6,7] that the release characteristics of pheromones depend primarily on two factors: (i) on material used for formulating pheromones, and (ii) on evaporative properties (e.g. vapor pressures, heats of vaporization and diffusion coefficients) of pheromones themselves. One convenient material that has been widely used is the rubber septum and its release characteristics have been studied in detail[5,8]. This material is supposed to exhibit first order emissive properties, which means that a linear dependence exists between the logarithm of pheromone concentration and time. On the other hand, only little is known at present about the fundamental physico-chemical characteristics of pheromones and pheromone blends. In spite of the fact that such properties can be established experimentally, it would be highly desirable to develop a simple computational method for predicting them, so as to facilitate selectin and optimization of pheromone formulations for a given purpose.

Our present aim is (i) to demonstrate that vapor pressures and heats of vaporization of pheromone-like acetates can be estimated from the known molecular structures by using group contribution methods and the corresponding states theory, and (ii) to check the validity of this concept by comparing predicted quantities with corresponding values obtained experimentally from independent measurements. Since sex pheromones of female *Lepidoptera* (C_{10} to C_{18} straight-chain unsaturated acetates) represent the largest group of insect behavior-modifying chemicals studied so far, they were used as data base for the predictions.

Nomenclature: The number of carbon atoms in the acetate chain is designed by an arabic numeral. Any unsaturation in the main chain is indicated by the geometry *Z* or *E* followed by its position(s) and separated from the number of carbon atoms by a hyphen. Thus e.g. (13*Z*)-13-octadecenyl acetate is designed as *Z*13-18 :OAc.

The data were processed on a Datron PC/XT personal computer using the linear least square regression program (Statgraphics Version 4·0).

RESULTS AND DISCUSSION

Thermodynamic properties correlations, developed in the past twenty years[9,10] and based on the principle of corresponding states, generally use three correlating parameters. A widely accepted[10] set of input data for estimating vapor pressures of pure liquids comprises the critical temperature T_c, the critical pressure P_c and the Pitzer's acentric factor ω. Although critical properties are of primary importance, their availability is severely limited. This can be illustrated by pointing out that published[10] T_c and P_c values for acetates are restricted only to those having three to seven carbon atoms. As a consequence, group contribution methods requiring only structural information are frequently used to obtain at least acceptable estimates.

Of the contribution methods proposed now to give reliable estimates of T_c and P_c, those of Fedors[11] (the original equation, $T_c = 535 \log (\sum \Delta_T)$, is used in a modified form viz. Eq. *1*, to give the best fit for the acetate series) and Ambrose[12] (Eqs (*2*) and (*3*)) were used in this work. In these methods the critical constants are estimated by using the following relations:

$$T_c = 517 \log (\textstyle\sum \Delta_T)\,, \qquad (1)$$

$$T_b = T_c/[1 + (1{\cdot}242 + \textstyle\sum \Delta_T)^{-1}]\,, \qquad (2)$$

$$P_c = M(0{\cdot}339 + \textstyle\sum \Delta_P)^{-2}\,, \qquad (3)$$

where T_b is the normal boiling point temperature, M is the molecular weight and $\sum\Delta$ quantities are evaluated by summing contributions for various atoms or group of atoms. The units employed are Kelvins, grams per moles and bars.

The resulting estimates of T_c, T_b and P_c are summarized in Table I. It is evident from the Table that all the parameters estimated are in reasonable agreement with the available experimental data, the maximum relative error in T_b not exceeding 1%. Additional support for the reliability of Eqs (*1*) to (*3*) comes from a comparison between estimated (Eqs (*4*) and (*5*)) and experimental vaporization enthalpies ΔH_v.

$$\Delta H_{vb} = 1{\cdot}093 \boldsymbol{R} T_c [T_{br}(\ln P_c - 1{\cdot}013)/(0{\cdot}930 - T_{br})] . \tag{4}$$

$$\Delta H_v = \Delta H_{vb}[(1 - T_r)/(1 - T_{br})]^{0.38} , \tag{5}$$

where $\boldsymbol{R}$ is the gas constant and $T_{br} = T_b/T_c$, $T_r = 298{\cdot}15/T_c$.

For ease of comparison with experimental data, ΔH_{vb} values based on Riedel's equation[14] (*4*) were scaled to the standard reference temperature of 298·15 K according[15] to the Watson's function (*5*). As shown in Table II, Eqs (*4*) and (*5*) permit a resonably accurate prediction of ΔH_v for all the acetates studied. It is to be noted that —CH_2— contribution to the ΔH_v values implied by Table II for the acetate homologous series is about 4·5 kJ/mol which is a slightly lower value than the commonly used general contribution (4·98 kJ/mol). On the other hand, a very similar value of 4·52 kJ/mol has been found experimentally for C_2 to C_4 acetates[17], while even lower value, 3·8 kJ/mol (ref.[18]) was proposed for high molecular weight sebacate and branched triglyceride ester series.

Based on results summarized in Tables I and II we suppose that Eqs (*1*) to (*3*) are sufficiently accurate so as the critical T_c and P_c estimates could be used in the next step.

To estimate vapor pressures of the compounds, the three parameter corresponding states equation of Lee and Kesler[19] (*6*) was employed here because it can be routinely implemented and its fundamental assumption are reliable.

$$\ln P_r = f^{(0)}(T_r) + \omega f^{(1)}(T_r) , \tag{6}$$

where P_r and T_r are the reduced pressure and temperature, the functions $f^{(0)}(T_r)$ and $f^{(1)}(T_r)$ are given by Eqs (*7*) and (*8*), and the acentric factor ω is obtained by applying Eq. (*6*) at the normal boiling point, i.e. by setting $T_r = T_b/T_c$ and $P_r = 1/P_c$ (P_c in atmospheres).

$$f^{(0)}(T_r) = 5{\cdot}92714 - 6{\cdot}09648/T_r - 1{\cdot}28862 \ln(T_r) + 0{\cdot}16935 T_r^6 \tag{7}$$

$$f^{(1)}(T_r) = 15{\cdot}2518 - 15{\cdot}6875/T_r - 13{\cdot}4721 \ln(T_r) + 0{\cdot}43577 T_r^6 \tag{8}$$

Following this approach, vapor pressures of fourteen linear acetates were calculated at 30°C. The results are summarized in Table III together with available experimental data. It is to be noted that the experimental vapor pressures given in this Table correspond to four different experimental techniques, i.e. (i) to the semi-micro method based upon restricted gas flow[20], (ii) to the "gas-saturation" method[6], (iii) to the gas chromatographic method using a cholesteryl-*p*-chlorocinnamate liquid crystal stationary phase[21,22], and (iv) to the gas chromatographic method using the substance under study as the stationary phase[23]. While data based on techniques (ii)–(iv) were obtained directly at 30°C, those of ref.[20] had to be extrapolated from

TABLE I

Calculated and experimental (in parentheses) T_c, T_b and P_c values of some C_2 to C_{12} acetates

Compound	T_c, K	P_c, MPa	T_b, K^b	Error, %^{c}
2 : OAc	522·3 (523·2)^a	3·985 (3·830)^a	347·40 (350·70)	−0·8
3 : OAc	549·9 (549·4)^a	3·480 (3·330)^a	373·90 (374·70)	−0·2
4 : OAc	574·5 (579·0)^a	3·090 (3·140)^a	398·40 (399·70)	−0·3
iso- -4 : OAc	566·7 (564·0)^a	3·109 (3·020)^a	390·68 (390·30)	+0·1
5 : OAc	596·7	2·777	421·18 (422·40)	−0·3
iso- -5 : OAc	589·6 (599·0)^a	2·793	414·00 (415·20)	−0·3
6 : OAc	616·8	2·523	442·50 (444·60)	−0·5
7 : OAc	635·3	2·311	462·51 (465·60)	−0·7
8 : OAc	652·4	2·131	481·38 (483·20)	−0·4
10 : OAc	683·2	1·845	516·13 (517·20)	−0·2
12 : OAc	710·2	1·627	547·51 543·20	+0·8

[a] Ref.[10]; [b] values in parentheses taken from ref.[13]; [c] error = $(T_b^{calc} - T_b^{exp}) \,.\, 100/T_b^{exp}$ %.

the temperature range at which they were measured (this temperature range gradually raises from 30 – 100°C for 6 : OAc to 150 – 200°C for 16 : OAc) to the temperature of interest. This extrapolation was carried out using the Antoine equation, with *A*, *B*, *C* coefficients taken from the compilation[24]. Since Antoine equation should not be used for temperatures outside the experimental range, the data of ref.[20] given in Table III have to be considered as only very approximate.

Of the methods mentioned above those based on GC measurements, being proposed[23] for the determination of vapor pressures in the range of 0·01 – 100 Pa with an experimental error of about ±2%, seem to be the most reliable. As demonstrated in Table III the agreement between calculated and GC based experimental data is rather good, given the broad range of pressures included (over 5 orders of magnitude). The mean relative error was found to be less than ±10% and in only two cases the error for an individual compound is around 20%. This represents a better accuracy than other experimental methods when compared among themselves.

At this point, we must comment on a defficiency in the calculation which arises in the treatment of isomeric alkenyl acetates. Since Eqs (*1*) – (*3*) do not account for different contributions to the critical quantities of positional as well as geometric

TABLE II

Calculated and experimental heats of vaporization $\Delta H_v(25°C)$ for some C_2 to C_{16} acetates

Compound	ΔH_v, kJ/mol			Error, %[c]
	Eq. (*4*)	Eq. (*5*)	Exp.[a]	
2 : OAc	31·88	35·02	35·14[b]	−0·3
3 : OAc	34·50	39·52	39·08[b]	+1·1
4 : OAc	37·04	43·96	43·60[b]	+0·8
10 : OAc	51·20	70·32	67·78	+3·7
11 : OAc	53·43	74·75	72·68	+2·8
12 : OAc	55·65	79·22	77·58	+2·1
13 : OAc	57·84	83·70	82·49	+1·5
14 : OAc	60·01	88·22	87·38	+1·0
15 : OAc	62·16	92·76	92·28	+0·5
16 : OAc	64·29	97·34	97·17	+0·2
*Z*7-10 : OAc	51·00	69·75	67·28	+3·6
*Z*7-12 : OAc	55·44	78·61	75·91	+3·5
*Z*9-14 : OAc	59·78	87·56	85·70	+2·2
*Z*11-16 : OAc	64·06	96·64	95·46	+1·2

[a] Unless otherwise stated taken from ref.[16]; [b] ref.[17]; [c] error = $(\Delta H_v^{calc} - \Delta H_v^{exp}) \,.\, 100/\Delta H_v^{exp}$ %.

TABLE III

Saturated vapor pressures (30°C) of some acetates

Compound	ω^a	P_{30}, Pa GS[b]	RGF[c]	GC[d]	Eq. (6)	Error, %[e]
6 : OAc	0·526		249·6		233·40	
8 : OAc	0·613		33·5		28·70	
9 : OAc	0·655	6·80			10·17	
10 : OAc	0·697		4·34	3·42 (3·66)	3·632	+6·2
11 : OAc	0·737			1·26	1·306	+3·6
12 : OAc	0·777	0·41	0·63	0·4633	0·463	+2·1
13 : OAc	0·816			0·1700	0·1730	+1·8
14 : OAc	0·854	0·12	0·16	0·0624	0·0635	+1·8
15 : OAc	0·891			0·0229	0·0235	+2·6
16 : OAc	0·928	0·056	0·051	0·0086	0·0088	+2·3
18 : OAc	0·998		0·0013		0·0013	
*Z*7-12 : OAc	0·766			0·5590 (0·5320)	0·5183	−7·2
*Z*9-14 : OAc	0·843	0·15		0·0877 (0·0900)	0·0697	−20·5
*Z*11-16 : OAc	0·917			0·0123	0·0097	−21·1

[a] Acentric factor from Eq. (6); [b] gas saturation method, ref.[6]; [c] restricted gas flow method, ref.[20]; [d] gas chromatographic method, refs[21,22] and ref.[23] (in parentheses); [e] error = $(P^{calc} - P^{exp}) \cdot 100/P^{exp}$ %, based on GC data from refs[21,22].

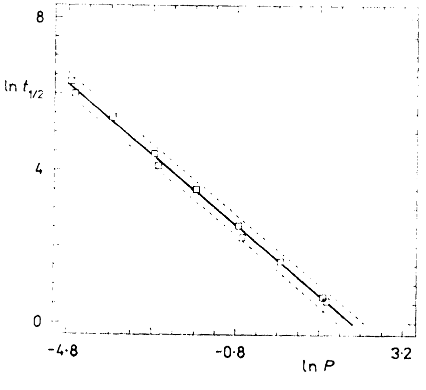

FIG. 1

Plot of the reported[16] half-lives of eleven acetates vs their calculated vapor pressures (30°C). The uncertainty is given as a 95% confidence interval (stroked lines)

(*E*)- and (*Z*)-isomers, likewise no differences in *P*-values for isomeric compounds can be expected. However, the scarce studies[6,23] addressing this problem indicate that vapor pressures of isomers usually fall in the narrow range, not very exceeding the experimental error. For example, vapor pressures of *Z*3-10 : OAc, *E*5-10 : OAc and *Z*6-10 : OAc at 30·4°C were estimated[23] as 4·65 ± 0·04 Pa, 4·08 ± 0·04 Pa and 4·38 ± 0·03 Pa, respectively. Therefore, we suppose that above limitation does not substantially change the validity of the calculation scheme.

Having obtained a significant correlation of the estimated *P* values with their experimental equivalents, we extended this study to evaluate a correlation of the calculated vapor pressures with first-order half-lives $t_{1/2}$ reported[16] for the evaporative loss of elven C_{10} to C_{16} acetates from rubber septa. The correlation equation corresponding to the linear least-squares curve fit (Fig. 1) is:

$$\ln t_{1/2} = (-0{\cdot}924 \pm 0{\cdot}016) \ln P + (1{\cdot}82 \pm 0{\cdot}04) \qquad (9)$$

with $n = 11$, $r = 0{\cdot}9986$ and the standard error of estimate $SE = 0{\cdot}11$.

The close correlation represented by Eq. (*9*) indicate that present calculations can be used to predict not only the vapor pressure but also the half-life for each compound. As an example of the use of this method some vaporization characteristics were predicted for three important[4] pheromone components of the *Lepidoptera ssp.* The results are shown in Table IV.

To summarize, the rather good agreement of calculated and experimental *P*, ΔH_v and $t_{1/2}$ data demonstrates impresively the validity of the concept presented in this paper, with application to modelling of the environmental fate of pheromone-like acetates. The relation found between vaporization properties and the chemical

TABLE IV

Predicted vaporization characteristics of some pheromone components

Acetates	*E*8,*E*10-12 : OAc[a]	*Z*13-18 : OAc[b]	*Z*3,*Z*13-18 : OAc[c]
T_b, K	575·4	625·8	624·9
T_c, K	712·4	776·8	777·6
P_c, MPa	1·715	1·223	1·247
P_{30}, Pa	0·570	0·001387	0·001527
ΔH_v^{25}, kJ/mol	78·00	105·8	105·1
$t_{1/2}^{30}$, days	10·4	2 698·6	2 469·1

[a] Pheromone component of *Laspeyresia pomonella, Laspeyresia nigricana, Phyacionia frustrana* etc.[4]; [b] pheromone component of *Cnaphalocrosis medinalis*[4]; [c] pheromone component of *Sessidae sp.*[4].

structures of the compounds indicate a general potential for this approach in studying vaporization phenomena in more complex systems containing mixtures of different classes of compounds. Further investigations on these possibilities are in progress.

APPENDIX

To illustrate the calculation scheme for estimating the vapor pressure of higher boiling acetates, we here apply it to tetradecyl acetate.

1) Using additive Δ_T Fedors increments[11]

$$\sum \Delta_T = (2)(\text{—CH}_3) + (13)(\text{—CH}_2\text{—}) + (1)(\text{—OCO—}) =$$
$$= (2)(1\cdot79) + (13)(1\cdot34) + 5\cdot32 = 26\cdot32$$

With Eq. (*1*), $T_c = 734\cdot3$ K.

2) Taking the increments quoted by Ambrose[12]

$$\sum \Delta_T = (15)(\text{C}) + (1)(\text{—OCO—}) = (15)(0\cdot138) + 0\cdot330 = 2\cdot4$$

With Eq. (*2*) and $T_c = 734\cdot3$ K, $T_b = 576\cdot1$ K.

$$\sum \Delta_P = (15)(\text{C}) + (1)(\text{—OCO—}) = (15)(0\cdot226) + 0\cdot47 = 3\cdot86$$

With Eq. (*3*) and $M = 256\cdot4$, $P_c = 1\cdot454$ MPa.

3) Lee–Kesler Eq. (*6*) is used to calculate acentric factor ω as $(\ln P_{rb} - f^{(0)})/f^{(1)}$. With $P_{rb} = P_b/P_c = 0\cdot101325/1\cdot454 = 0\cdot06969$ and $T_{rb} = T_b/T_c = 576\cdot1/734\cdot3 = 0\cdot78456$, $\omega = 0\cdot85427$.

4) We now calculate P_r^{30} with $T_r = 303\cdot15/734\cdot3 = 0\cdot4128$ using Eq. (*6*) and parameters calculated above

$$P_r^{30} = 4\cdot36651 \,.\, 10^{-8}$$
$$P^{30} = P_c \,.\, P_r^{30} = 1\cdot454 \,.\, 10^6 \,.\, 4\cdot36651 \,.\, 10^{-8} = 0\cdot06349 \text{ Pa}$$

The experimental vapor pressure at 30°C is reported[21] as 0·0624 Pa; therefore the error is about 1·8%.

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