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CALCULATION OF PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY CHARACTERISTICS FROM ISOTHERMAL DATA

II. PREDICTED RETENTION TIMES AND ELUTION TEMPERATURES

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SUMMARY

Theoretical procedures, described in Part I, *J. Chromatogr.*, 405 (1987) 67-76, for predicting retention times and elution temperatures in programmed temperature gas chromatography from isothermal data are experimentally tested for a number of compounds under a range of experimental conditions. In general, and taking into full consideration random error predictions, agreement is reasonably satisfactory.

INTRODUCTION

Part I¹ describes theoretical and computational procedures for predicting programmed-temperature gas chromatography (PTGC) characteristics using, as input information, experimental data for the same column and carrier gas pressure differential but obtained under isothermal gas chromatographic (IGC) conditions. Of the various types of PTGC data, perhaps the most important (for reasons presented in Part I¹) are retention times and elution temperatures. These have been predicted for a range of organic compounds (*n*-alkanes, monocyclic aromatic hydrocarbons and ketones) on a capillary column under a variety of programmed-temperature conditions. The present paper describes the comparison of theoretical and experimental results for several values of (a) column temperature at sample injection (initial temperature), and (b) rate of column heating (heating rate); the temperature programme corresponds in each case to a linear increase of temperature with time (single linear ramp). Random error in (isothermal) input data (in some cases derived by standard statistical methodology from graphical plots, in others based on manufacturer's specifications, in others estimated) has been incorporated into the calculations to make comparison of theory and experiment more meaningful.

A further manuscript², to be submitted for publication, will make similar comparisons for retention indices and will compare two kinds of equivalent

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temperatures¹ with various averages of initial and elution temperatures and with the Giddings significant temperature³.

EXPERIMENTAL

The gas chromatograph used was a Hewlett-Packard (HP) Model 5792A (with facilities for both IGC and PTGC operation) fitted with an HP 7671A automatic sampler. It was operated with an HP Ultra 2 capillary column (25 m × 0.2 mm I.D. fused-silica coated with a 0.33- μ m layer of cross-linked 5% phenylmethylsilicone) with split mode injection (0.5% of the sample entering the column) and a hydrogen flame ionisation detector. The flow of nitrogen carrier gas was controlled by a constant mass-flow device and a column pressure regulator; column flow-rate was of the order of 1 cm³ min⁻¹, but this varied with column temperature.

Compounds studied were purchased from Aldrich, Eastman-Kodak, BDH or Fluka; they were of high purity (98–99.9%) and used without further purification. For chromatographic purposes, solutions were made by dissolving 50 mm³ of each compound in 25 cm³ of dichloromethane, and preset volumes of 1 mm³ were injected, either manually or via the automatic sampler, into the chromatograph. A list of compounds studied is given in the first column of Table I.

Twelve replicate isothermal runs were performed for each compound at 393.16, 403.16, 413.16 and 423.16 K. Programmed temperature runs were conducted under a variety of combinations of initial absolute temperature, T_i (oven temperature at sample injection), and oven heating rate, k_3 (the symbolism corresponds to that used in

TABLE I
LIST OF COMPOUNDS STUDIED AND THEIR ISOTHERMAL RETENTION TIMES

Values in parenthesis are 95% confidence deviations.

Compound	Retention time/s at temperature/K			
	393.16	403.16	413.16	423.16
<i>n</i> -Nonane	136.6 (0.0)	126.7 (0.0)	119.5 (0.0)	114.7 (0.0)
<i>n</i> -Decane	177.8 (0.0)	156.4 (0.1)	141.8 (0.0)	131.2 (0.0)
<i>n</i> -Undecane	250.9 (0.1)	207.8 (0.1)	178.3 (0.0)	158.1 (0.0)
<i>n</i> -Dodecane	379.4 (0.1)	295.5 (0.1)	239.3 (0.0)	201.5 (0.0)
<i>n</i> -Tridecane	609.1 (0.0)	447.4 (0.2)	342.2 (0.0)	272.8 (0.0)
<i>n</i> -Tetradecane	1011.5 (0.1)	706.2 (0.4)	512.4 (0.2)	387.7 (0.1)
<i>n</i> -Pentadecane	1720.6 (0.1)	1147.6 (0.1)	795.0 (0.0)	573.4 (0.2)
Nonan-5-one	228.9 (0.0)	192.8 (0.1)	168.1 (0.1)	151.0 (0.1)
Propiophenone	344.6 (0.1)	275.8 (0.1)	228.6 (0.0)	196.3 (0.1)
Butyrophenone	505.6 (0.1)	385.9 (0.1)	305.4 (0.1)	250.7 (0.1)
Valerophenone	827.3 (0.0)	599.3 (0.2)	450.3 (0.1)	351.5 (0.1)
Hexanophenone	1393.1 (0.2)	963.8 (0.3)	690.3 (0.2)	513.7 (0.1)
Isopropyl benzoate	405.9 (0.1)	316.6 (0.1)	256.1 (0.1)	215.2 (0.1)
2-Phenylpropane	151.3 (0.1)	138.2 (0.0)	128.8 (0.0)	122.2 (0.0)
1-Phenylpropane	163.6 (0.1)	147.3 (0.0)	135.6 (0.0)	127.4 (0.1)
1-Phenylbutane	224.9 (0.0)	191.6 (0.1)	168.1 (0.1)	151.8 (0.0)
1-Phenylpentane	330.7 (0.1)	265.8 (0.1)	221.0 (0.1)	190.4 (0.0)
1-Phenyloctane	1430.5 (0.0)	984.9 (0.1)	701.9 (0.2)	519.9 (0.1)

TABLE II

INTERCEPTS ($\ln k_1$) AND GRADIENTS (k_2) OF LEAST SQUARES PLOTS OF $\ln k'$ AGAINST T^{-1}

Values in parenthesis are standard deviations.

Compound	$\ln k_1$	k_2/K	Covariance
<i>n</i> -Nonane	-11.12 (0.06)	4190 (40)	-2.4
<i>n</i> -Decane	-11.80 (0.06)	4690 (20)	-1.2
<i>n</i> -Undecane	-12.39 (0.03)	5140 (10)	-0.3
<i>n</i> -Dodecane	-13.08 (0.02)	5640 (10)	-0.2
<i>n</i> -Tridecane	-13.62 (0.10)	6070 (50)	-5.0
<i>n</i> -Tetradecane	-15.44 (0.60)	7040 (200)	-120
<i>n</i> -Pentadecane	-15.01 (0.08)	7070 (30)	-2.4
Nonan-5-one	-12.09 (0.02)	5000 (10)	-0.2
Propiophenone	-12.07 (0.04)	5190 (20)	-0.8
Butyrophenone	-12.56 (0.04)	5570 (20)	-0.8
Valerophenone	-13.26 (0.04)	6070 (20)	-0.8
Hexanophenone	-14.00 (0.05)	6580 (20)	-1.0
Isopropyl benzoate	-12.58 (0.02)	5470 (10)	-0.2
2-Phenylpropane	-10.76 (0.07)	4150 (30)	-2.1
1-Phenylpropane	-10.89 (0.04)	4260 (20)	-0.8
1-Phenylbutane	-11.46 (0.08)	4710 (30)	-2.4
1-Phenylpentane	-12.13 (0.09)	5190 (30)	-2.7
1-Phenyloctane	-13.98 (0.05)	6580 (20)	-1.0

TABLE III

COMPARISON OF OBSERVED AND PREDICTED PTGC RETENTION TIMES AT A HEATING RATE OF 2.00 K min⁻¹

Compound	Retention time/K					
	Initial temperature 333.16 K			Initial temperature 393.16 K		
	Predicted*		Observed**	Predicted*		Observed**
	(1)	(2)		(1)	(2)	
<i>n</i> -Nonane	334 (13)	332 (13)	360.0 (0.2)	133 (2)	133 (2)	133.2 (0.1)
<i>n</i> -Decane	567 (2)	564 (3)	594.0 (0.1)	170 (1)	171 (1)	169.8 (0.1)
<i>n</i> -Undecane	875 (3)	872 (2)	900.4 (0.1)	229 (1)	230 (1)	230.4 (0.1)
<i>n</i> -Dodecane	1270 (6)	1268 (6)	1296.4 (0.1)	327 (1)	329 (1)	326.4 (0.1)
<i>n</i> -Tridecane	1666 (23)	1666 (23)	1680.4 (0.1)	466 (8)	468 (8)	468.6 (0.1)
<i>n</i> -Tetradecane	2149 (52)	2150 (51)	2087.9 (0.1)	677 (45)	679 (44)	661.2 (0.1)
<i>n</i> -Pentadecane	2480 (9)	2483 (9)	2466.4 (0.1)	906 (4)	910 (4)	901.2 (0.1)
Nonan-5-one	826 (5)	823 (4)	828.4 (0.1)	222 (1)	223 (1)	213.0 (0.1)
Propiophenone	1124 (10)	1122 (10)	1140.2 (0.1)	303 (2)	304 (2)	303.6 (0.1)
Butyrophenone	1471 (11)	1470 (10)	1500.3 (0.0)	411 (3)	413 (3)	414.0 (0.1)
Valerophenone	1904 (11)	1905 (11)	1911.8 (0.0)	591 (4)	593 (4)	589.2 (0.1)
Hexanophenone	2314 (8)	2317 (8)	2321.9 (0.1)	814 (2)	818 (1)	816.2 (0.1)
Isopropyl benzoate	1286 (6)	1284 (6)	1320.4 (0.1)	344 (1)	345 (1)	345.8 (0.0)
2-Phenylpropane	394 (5)	392 (5)	413.8 (0.2)	147 (1)	148 (0)	146.6 (0.1)
1-Phenylpropane	450 (6)	447 (6)	480.3 (0.2)	157 (1)	158 (1)	157.8 (0.0)
1-Phenylbutane	730 (4)	727 (4)	774.2 (0.1)	210 (1)	211 (1)	210.6 (0.1)
1-Phenylpentane	1089 (5)	1087 (4)	1134.4 (0.1)	291 (3)	293 (3)	293.4 (0.1)
1-Phenyloctane	2328 (8)	2331 (8)	2340.1 (0.1)	824 (2)	827 (1)	829.2 (0.1)

* Columns (1) and (2) refer to calculations using eqns. 1 and 2, respectively, for the column dead time dependence upon temperature. Values in parentheses are estimated standard deviations.

** Values in parentheses are 95% confidence deviations.

Part I¹); the assumption is made in this work that the column temperature exactly matches that of the oven. All combinations of T_i of 333.16, 353.16, 373.16 and 393.16 K, and k_3 of 1.00, 2.00, 3.00, 5.00, 7.00, 10.00, 12.00 and 15.00 K min⁻¹ have been used for each of twelve replicate runs on each compound.

Data acquisition was accomplished by a Trivector Trilab 2500 data system connected to the chromatograph via an A/D converter. A BBC Model B micro-computer, interfaced to the data system, was used to perform calculations on the acquired data via BASIC programs.

EXPERIMENTAL AND PREDICTED RESULTS

Mean retention times t_R for isothermal runs are presented in Table I, together with 95% confidence deviations (in parentheses). Times for the seven *n*-alkanes have been used to evaluate column dead times, t_0 , at the four temperatures, on the BBC Computer, by the method of Al-Thamir *et al.*⁴. These column dead times were then used to (a) calculate capacity factors, k' , from the isothermal retention times ($k' =$

TABLE IV

COMPARISON OF OBSERVED AND PREDICTED PTGC RETENTION TIMES AT A HEATING RATE OF 7.00 K min⁻¹

Compound	Retention time/s					
	Initial temperature 333.16 K			Initial temperature 393.16 K		
	Predicted*		Observed**	Predicted*		Observed**
	(1)	(2)		(1)	(2)	
<i>n</i> -Nonane	263 (7)	262 (7)	270.0 (0.0)	128 (2)	128 (2)	127.4 (0.1)
<i>n</i> -Decane	379 (1)	378 (1)	378.0 (0.0)	158 (1)	158 (1)	155.9 (0.1)
<i>n</i> -Undecane	503 (1)	503 (1)	508.0 (0.1)	200 (1)	201 (0)	199.4 (0.1)
<i>n</i> -Dodecane	639 (2)	640 (2)	636.0 (0.1)	261 (1)	263 (1)	259.2 (0.1)
<i>n</i> -Tridecane	765 (6)	766 (6)	763.8 (0.1)	335 (3)	337 (4)	333.6 (0.1)
<i>n</i> -Tetradecane	894 (24)	896 (24)	884.4 (0.1)	421 (23)	423 (23)	421.8 (0.0)
<i>n</i> -Pentadecane	1004 (2)	1005 (2)	999.0 (0.1)	516 (2)	518 (2)	516.0 (0.1)
Nonan-5-one	487 (2)	487 (2)	474.0 (0.2)	196 (1)	197 (0)	187.4 (0.1)
Propiophenone	600 (3)	601 (3)	603.6 (0.1)	250 (1)	251 (1)	247.8 (0.1)
Butyrophenone	715 (3)	716 (3)	717.0 (0.1)	312 (2)	313 (1)	312.0 (0.1)
Valerophenone	847 (3)	849 (2)	845.4 (0.1)	398 (2)	400 (2)	396.0 (0.1)
Hexanophenone	966 (1)	968 (1)	966.0 (0.2)	489 (1)	491 (1)	492.0 (0.0)
Isopropyl benzoate	651 (2)	652 (1)	654.0 (0.0)	273 (1)	274 (1)	273.0 (0.1)
2-Phenylpropane	298 (3)	297 (2)	304.2 (0.0)	140 (0)	140 (0)	139.2 (0.1)
1-Phenylpropane	327 (3)	327 (3)	336.0 (0.0)	148 (1)	148 (1)	147.8 (0.1)
1-Phenylbutane	454 (1)	454 (1)	456.0 (0.0)	188 (1)	189 (1)	187.2 (0.1)
1-Phenylpentane	587 (3)	587 (2)	589.8 (0.0)	242 (2)	243 (2)	241.8 (0.1)
1-Phenyloctane	971 (1)	973 (1)	968.4 (0.1)	493 (1)	495 (1)	495.0 (0.1)

* Columns (1) and (2) refer to calculations using eqns. 1 and 2, respectively, for the column dead time dependence upon temperature. Values in parentheses are estimated standard deviations.

** Values in parentheses are 95% confidence deviations.

TABLE V

COMPARISON OF OBSERVED AND PREDICTED PTGC RETENTION TIMES AT A HEATING RATE OF 15.00 K min⁻¹

Compound	Retention time/s					
	Initial temperature 333.16 K			Initial temperature 393.16 K		
	Predicted*		Observed**	Predicted*		Observed**
	(1)	(2)		(1)	(2)	
<i>n</i> -Nonane	211 (4)	211 (4)	212.8 (0.1)	122 (1)	123 (1)	121.0 (0.1)
<i>n</i> -Decane	276 (1)	277 (1)	274.7 (0.1)	145 (1)	145 (1)	142.2 (0.1)
<i>n</i> -Undecane	341 (1)	342 (0)	339.6 (0.0)	174 (1)	175 (1)	171.6 (0.1)
<i>n</i> -Dodecane	408 (1)	409 (1)	403.7 (0.1)	212 (1)	213 (0)	209.1 (0.1)
<i>n</i> -Tridecane	469 (3)	470 (3)	465.5 (0.1)	255 (2)	256 (2)	252.7 (0.1)
<i>n</i> -Tetradecane	525 (14)	526 (14)	524.1 (0.1)	297 (14)	298 (14)	298.3 (0.1)
<i>n</i> -Pentadecane	581 (2)	582 (2)	579.8 (0.1)	349 (2)	350 (1)	349.1 (0.1)
Nonan-5-one	334 (1)	334 (1)	323.5 (0.1)	171 (1)	172 (0)	164.2 (0.1)
Propiophenone	393 (1)	394 (1)	390.4 (0.0)	207 (1)	208 (1)	204.4 (0.1)
Butyrophenone	449 (1)	450 (1)	446.0 (0.2)	244 (1)	245 (1)	241.5 (0.1)
Valcrophenone	512 (1)	513 (1)	508.8 (0.1)	292 (1)	293 (1)	289.7 (0.1)
Hexanophenone	567 (1)	569 (1)	568.2 (0.0)	338 (1)	340 (1)	340.3 (0.0)
Isopropyl benzoate	417 (1)	418 (1)	414.2 (0.1)	221 (1)	222 (0)	218.4 (0.1)
2-Phenylpropane	234 (1)	233 (1)	233.3 (0.2)	132 (0)	133 (0)	128.8 (0.1)
1-Phenylpropane	250 (2)	250 (2)	251.7 (0.1)	138 (1)	139 (0)	135.3 (0.1)
1-Phenylbutane	319 (1)	319 (0)	317.8 (0.0)	167 (1)	168 (0)	163.0 (0.1)
1-Phenylpentane	386 (2)	387 (2)	383.6 (0.1)	202 (2)	203 (1)	198.3 (0.1)
1-Phenyloctane	570 (1)	571 (1)	569.4 (0.0)	341 (1)	342 (1)	339.1 (0.1)

* Columns (1) and (2) refer to calculations using eqns. 1 and 2, respectively, for the column dead time dependence upon temperature. Values in parentheses are estimated standard deviations.

** Values in parentheses are 95% confidence deviations.

$t_R/t_0 - 1$), and (b) determine least squares linear relationships between t_0 and absolute temperature T (assumed free of measurement error) and between t_0 and the square root of T (together with the standard deviation of the pairs of coefficients and their covariances). The equations obtained for (b) were

$$t/s = 22.96 (1.86) + 0.1525 (0.0046)T/K; \quad \text{covariance } -0.0085 \quad (1)$$

$$t/s = -46.4 (3.6) + 6.54 (0.179) \sqrt{T/K}; \quad \text{covariance } -0.64 \quad (2)$$

(statistical deviations, standard or 95% confidence, are given in parentheses throughout the paper). On the basis of an expectation that $\ln k'$ is a linear function of T^{-1} (see Part I¹), least squares methodology was used to obtain regression coefficients for each of the compounds studied, together with standard deviations and covariance. These values are presented in Table II; in conformation with the notation used in Part I, the constant and the multiplier of T^{-1} are designated $\ln k_1$ and k_2 .

TABLE VI

COMPARISON OF OBSERVED AND PREDICTED PTGC ELUTION TEMPERATURES AT A HEATING RATE OF 2.00 K min^{-1}

Compound	Elution temperature/K					
	Initial temperature 333.16 K			Initial temperature 393.16 K		
	Predicted*		Observed**	Predicted*		Observed**
	(1)	(2)		(1)	(2)	
<i>n</i> -Nonane	344.3 (0.5)	344.2 (0.4)	345.0	397.6 (0.1)	397.6 (0.1)	397.4
<i>n</i> -Decane	352.1 (0.1)	352.0 (0.1)	353.0	398.8 (0.1)	398.9 (0.1)	398.7
<i>n</i> -Undecane	362.3 (0.1)	362.2 (0.1)	363.8	400.8 (0.1)	400.8 (0.1)	400.7
<i>n</i> -Dodecane	375.5 (0.2)	375.4 (0.2)	376.4	404.1 (0.1)	404.1 (0.1)	403.9
<i>n</i> -Tridecane	388.7 (0.8)	388.7 (0.8)	389.6	408.7 (0.3)	408.8 (0.3)	408.6
<i>n</i> -Tetradecane	404.8 (1.7)	404.8 (1.7)	402.7	415.7 (1.5)	415.8 (1.5)	415.0
<i>n</i> -Pentadecane	415.8 (0.2)	415.9 (0.1)	415.4	423.4 (0.2)	423.5 (0.2)	423.0
Nonan-5-one	360.7 (0.2)	360.6 (0.2)	360.6	400.6 (0.1)	400.6 (0.1)	400.1
Propiophenone	370.6 (0.3)	370.5 (0.3)	371.7	403.3 (0.1)	403.3 (0.1)	403.0
Butyrophenone	382.2 (0.4)	382.2 (0.3)	383.1	406.9 (0.1)	406.9 (0.1)	406.7
Valcrophenone	396.6 (0.3)	396.7 (0.3)	396.9	412.8 (0.2)	412.9 (0.2)	412.6
Hexanophenone	410.3 (0.1)	410.3 (0.1)	410.3	420.3 (0.1)	420.4 (0.1)	420.2
Isopropyl benzoate	376.0 (0.2)	376.0 (0.2)	377.3	404.6 (0.1)	404.7 (0.1)	404.5
2-Phenylpropane	346.3 (0.2)	346.3 (0.2)	346.9	398.1 (0.0)	398.1 (0.0)	397.9
1-Phenylpropane	348.2 (0.2)	348.1 (0.2)	349.1	398.4 (0.1)	398.4 (0.0)	398.2
1-Phenylbutane	357.5 (0.2)	357.4 (0.2)	358.8	400.2 (0.1)	400.2 (0.1)	400.0
1-Phenylpentane	369.5 (0.2)	369.4 (0.2)	370.8	402.9 (0.1)	402.9 (0.1)	402.7
1-Phenyloctane	410.8 (0.1)	410.8 (0.1)	411.0	420.6 (0.1)	420.7 (0.1)	420.6

* Columns (1) and (2) refer to calculations using eqns. 1 and 2, respectively, for the column dead time dependence upon temperature. Values in parentheses are estimated standard deviations.

** 95% Confidence deviations are all less than 0.1.

Using the theoretical and computational techniques described in Part I, retention times, t_R , and elution temperatures, T_e (with their standard deviations) have been calculated for the various programmed temperature conditions given above; initial temperature standard deviations have been taken as 0.03 K (in accordance with manufacturer's specifications) and heating rate standard deviations have been estimated as 0.01 K min^{-1} . Comparison of these predictions and corresponding values obtained by experiment (with 95% confidence deviations for retention times) are shown in Tables III–VIII for a selection of PTGC experimental conditions; a comprehensive set of tables covering all 32 combinations of experimental conditions may be obtained from the authors.

The effect of *individual* random errors in the input data for the calculations has been analysed. Four separate factors have been considered (a) standard deviations and covariances of the pairs of coefficients in the column dead time vs. temperature relationships, (b) initial temperature standard deviation, (c) heating rate standard deviation, (d) standard deviations and covariance of the pair of coefficients in the $\ln k'$ vs. T^{-1} relationship. *Individual* resultant contributions to predicted standard devia-

TABLE VII

COMPARISON OF OBSERVED AND PREDICTED PTGC ELUTION TEMPERATURES AT A HEATING RATE OF 7.00 K min⁻¹

Compound	Elution temperature/K					
	Initial temperature 333.16 K			Initial temperature 393.16 K		
	Predicted*		Observed**	Predicted*		Observed**
	(1)	(2)		(1)	(2)	
<i>n</i> -Nonane	363.8 (0.9)	363.7 (0.9)	364.8	408.1 (0.2)	408.1 (0.2)	407.9
<i>n</i> -Decane	377.4 (0.1)	377.3 (0.2)	377.8	411.6 (0.1)	411.6 (0.1)	411.2
<i>n</i> -Undecane	391.9 (0.1)	391.9 (0.1)	392.3	416.5 (0.1)	416.6 (0.1)	416.2
<i>n</i> -Dodecane	407.7 (0.2)	407.8 (0.2)	407.5	423.6 (0.1)	423.8 (0.1)	423.1
<i>n</i> -Tridecane	422.4 (0.7)	422.5 (0.7)	422.1	432.3 (0.4)	432.5 (0.4)	431.9
<i>n</i> -Tetradecane	437.5 (2.8)	437.7 (2.8)	436.2	442.3 (2.6)	442.5 (2.6)	442.0
<i>n</i> -Pentadecane	450.2 (0.2)	450.5 (0.2)	449.6	453.4 (0.3)	453.6 (0.2)	453.0
Nonan-5-one	390.0 (0.2)	390.0 (0.2)	388.7	416.0 (0.1)	416.1 (0.1)	414.9
Propiophenone	403.2 (0.4)	403.2 (0.4)	403.3	422.3 (0.2)	422.4 (0.1)	421.9
Butyrophenone	416.6 (0.3)	416.7 (0.3)	416.4	429.5 (0.2)	429.7 (0.2)	429.1
Valerophenone	432.0 (0.3)	432.2 (0.3)	431.3	439.6 (0.2)	439.8 (0.2)	439.2
Hexanophenone	445.9 (0.1)	446.1 (0.0)	445.6	450.2 (0.1)	450.0 (0.1)	450.3
Isopropyl benzoate	409.1 (0.2)	409.2 (0.2)	409.3	425.0 (0.1)	425.1 (0.1)	424.8
2-Phenylpropane	368.0 (0.3)	367.9 (0.3)	368.5	409.5 (0.1)	409.5 (0.0)	409.2
1-Phenylpropane	371.4 (0.3)	371.3 (0.4)	372.3	410.4 (0.1)	410.5 (0.1)	410.2
1-Phenylbutane	386.1 (0.1)	386.1 (0.1)	386.8	415.1 (0.1)	415.2 (0.1)	414.8
1-Phenylpentane	401.6 (0.3)	401.7 (0.3)	401.9	421.4 (0.2)	421.5 (0.2)	421.2
1-Phenyloctane	446.4 (0.1)	446.7 (0.1)	446.1	450.7 (0.1)	450.9 (0.1)	450.7

* Columns (1) and (2) refer to calculations using eqns. 1 and 2, respectively, for the column dead time dependence upon temperature. Values in parentheses are estimated standard deviations.

** 95% Confidence deviations are all less than 0.1.

tions of retention times and elution temperatures (together with total standard deviations) are presented in Tables IX and X for two compounds *n*-decane and *n*-tetradecane, using the column dead time eqn. 1 (results for eqn. 2 are very similar) and four PTGC experimental conditions. The latter compound has very large contributions to (d), as indicated in Table II; the former is much more "typical" of the compounds studied here.

DISCUSSION

The results presented in Tables IX and X indicate the possibility of a substantial prediction error contribution from the assumption of a linear relationship between $\ln k'$ and T^{-1} , but the case of *n*-tetradecane is exceptional (as Table II indicates) in the compounds studied here. Generally, there is no clear general predominance of one particular contributions to overall predicted error, although there may be some uncertainty about the chosen standard deviations for initial temperature and heating rate, particularly for the latter. The overall fractional errors for predicted elution

TABLE VIII

COMPARISON OF OBSERVED AND PREDICTED PTGC ELUTION TEMPERATURES AT A HEATING RATE OF 15.00 K min⁻¹

Compound	Elution temperature/K					
	Initial temperature 333.16 K			Initial temperature 393.16 K		
	Predicted*		Observed**	Predicted*		Observed**
	(1)	(2)		(1)	(2)	
<i>n</i> -Nonane	385.9 (1.1)	385.8 (1.1)	386.2	423.6 (0.3)	423.8 (0.3)	423.2
<i>n</i> -Decane	402.2 (0.2)	402.3 (0.2)	401.7	429.3 (0.2)	429.5 (0.1)	428.5
<i>n</i> -Undecane	418.4 (0.2)	418.6 (0.1)	417.9	436.6 (0.1)	436.9 (0.1)	435.9
<i>n</i> -Dodecane	435.1 (0.2)	435.4 (0.1)	433.9	446.2 (0.1)	446.5 (0.1)	445.3
<i>n</i> -Tridecane	450.3 (0.6)	450.6 (0.6)	449.4	457.0 (0.4)	457.3 (0.4)	456.2
<i>n</i> -Tetradecane	464.3 (3.6)	464.6 (3.6)	464.0	467.5 (3.5)	467.8 (3.4)	467.8
<i>n</i> -Pentadecane	478.3 (0.4)	478.7 (0.3)	477.9	480.4 (0.4)	480.7 (0.4)	480.3
Nonan-5-one	416.6 (0.2)	416.7 (0.2)	413.9	436.0 (0.1)	436.2 (0.1)	434.2
Propiophenone	431.4 (0.4)	431.6 (0.3)	430.6	444.9 (0.2)	445.2 (0.2)	444.3
Butyrophenone	445.4 (0.3)	445.7 (0.3)	444.5	454.2 (0.2)	454.5 (0.2)	453.6
Valerophenone	461.1 (0.3)	461.4 (0.2)	460.2	466.1 (0.2)	466.4 (0.2)	465.6
Hexanophenone	475.0 (0.2)	475.3 (0.1)	475.1	477.8 (0.2)	478.1 (0.2)	478.3
Isopropyl benzoate	437.3 (0.2)	437.5 (0.1)	436.6	448.3 (0.1)	448.6 (0.1)	447.6
2-Phenylpropane	391.6 (0.3)	391.5 (0.3)	391.3	426.1 (0.1)	426.3 (0.0)	425.3
1-Phenylpropane	395.8 (0.4)	395.7 (0.4)	395.9	427.6 (0.1)	427.8 (0.1)	427.0
1-Phenylbutane	412.9 (0.1)	413.0 (0.0)	412.6	434.8 (0.2)	435.1 (0.2)	433.9
1-Phenylpentane	429.6 (0.4)	429.8 (0.4)	429.0	443.7 (0.4)	444.0 (0.4)	442.7
1-Phenyloctane	475.6 (0.2)	475.9 (0.1)	475.4	478.3 (0.2)	478.7 (0.1)	478.0

* Columns (1) and (2) refer to calculations using eqns. 1 and 2, respectively, for the column dead time dependence upon temperature. Values in parentheses are estimated standard deviations.

** 95% Confidence deviations are all less than 0.1.

temperatures are considerably smaller than those for predicted retention times, but this is as expected on the basis of the interrelationship between these two quantities, *viz.*, $T_e - T_i = k_3 t_R$. On the basis of error-free k_3 , the fractional errors in t_R and $T_e - T_i$ will be equal, and the fractional error in T_e will be a fraction $(1 - T_i/T_e)$ of this.

The agreement between predicted and experimental parameters as indicated by the selected data of Tables III–VIII (and by the more comprehensive data available to the authors) is generally reasonably satisfactory (particularly bearing in mind the predicted standard errors; generally, errors in the experimental PTGC parameters can be discounted in comparison). In some cases, *absolute* differences are substantial but these normally apply to high retention times; *fractional* differences [(experimental – predicted)/experimental] are probably a more realistic indicator of the quality of the predictions. Two generalisations have been made: (a) where there is a substantial difference, observed parameters are usually larger than predicted ones; (b) fractional differences generally decrease with increasing initial temperature and with increasing heating rate.

The difference in pairs of predictions for the two column dead time formulae

TABLE IX
INDIVIDUAL CONTRIBUTIONS TO STANDARD DEVIATIONS OF RETENTION TIMES

Compound	Heating rate/ $K \text{ min}^{-1}$	Retention time error/s*									
		$T_i = 333.16 \text{ K}$					$T_i = 393.16 \text{ K}$				
		a	b	c	d	Total	a	b	c	d	Total
<i>n</i> -Decane	2.00	1.8	0.4	0.7	0.7	2.1	0.4	0.1	0.0	0.8	0.9
<i>n</i> -Decane	10.00	0.6	0.1	0.1	0.7	1.0	0.3	0.0	0.0	0.6	0.7
<i>n</i> -Tetradecane	2.00	1.9	0.9	7.3	51.0	51.6	1.2	0.5	1.0	45.4	45.4
<i>n</i> -Tetradecane	10.00	0.6	0.2	0.5	18.3	18.3	0.6	0.1	0.2	18.5	18.5

* Standard error contributions from: (a) column dead time-temperature relationship, (b) initial temperature, (c) heating rate, (d) $\ln(\text{capacity factor})$ -temperature relationship.

(eqns. 1 and 2) is generally small, never more than 4 s for retention times, and well within predictive error, suggesting that two-coefficient formulae are adequate. On the other hand, the formulae have been obtained (because of the experimental necessity of obtaining reasonably short IGC retention times) over a rather different temperature range (393–423 K) than those covered in PTGC experiments; the same point in fact applies to coefficients in the $\ln k'$ vs. T^{-1} linear relationships. This might well be a contributory factor to the differences between experimental and predicted parameters. Other contributory factors might be: (a) inadequacy of the methodology used⁴ to determine column dead times, this being formally dependent upon a linear relationship between molar Gibbs energy of solution in the stationary phase and carbon number of the *n*-alkanes; (b) variation of molar enthalpies and entropies of solution with temperature, causing some deviation from linearity of $\ln k'$ and T^{-1} (such a temperature dependence has in fact been considered by others⁵); (c) a temperature time lag between column and oven (see, *e.g.*, ref. 6), although this factor will clearly be more significant for packed columns; (d) non-instantaneous transfer of solute from injection port to column and non-instantaneous cooling from port to initial column temperature.

TABLE X
INDIVIDUAL CONTRIBUTIONS TO STANDARD DEVIATIONS OF ELUTION TEMPERATURES

Compound	Heating rate/ $K \text{ min}^{-1}$	Elution temperature error/K*									
		$T_i = 333.16 \text{ K}$					$T_i = 393.16 \text{ K}$				
		a	b	c	d	Total	a	b	c	d	Total
<i>n</i> -Decane	2.00	0.06	0.02	0.07	0.02	0.10	0.01	0.03	0.03	0.03	0.05
<i>n</i> -Decane	10.00	0.11	0.01	0.03	0.12	0.16	0.06	0.02	0.02	0.11	0.12
<i>n</i> -Tetradecane	2.00	0.06	0.00	0.11	1.70	1.70	0.04	0.01	0.08	1.51	1.52
<i>n</i> -Tetradecane	10.00	0.09	0.00	0.03	3.05	3.05	0.11	0.01	0.03	3.08	3.08

* Standard error contributions from: (a) column dead time-temperature relationship, (b) initial temperature, (c) heating rate, (d) $\ln(\text{capacity factor})$ -temperature relationship.

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