For the titrations in which KCl was not added, the ionic strength was estimated and thermodynamic values for pK_a were calculated from the equations (*1*)

$$pK^{T}_{a_1} = pK_{a_1} + \frac{0.505\,(\mu)^{1/2}}{1 + 1.6\,(\mu)^{1/2}}$$

and

$$pK^{T}_{a_2} = pK_{a_2} + \frac{1.515\,(\mu)^{1/2}}{1 + 1.6\,(\mu)^{1/2}}$$

RESULTS AND DISCUSSION

The calculated values of the ionization constants are listed in Table I. The precision of the pK_a values is the standard deviation of five sets of two data points for each titration. In the case of the solutions in which KCl was added, the constants are concentration- and ionic strength-dependent, and are not thermodynamic values. Since the Debye-Hückel law does not hold in solutions of high ionic strength, no corrections were attempted.

The results of the titration at 28.2° C. in which no KCl was added ($K_{a_1} = 5.90 \times 10^{-2}$ and $K_{a_2} = 2.93 \times 10^{-3}$) are similar to those reported by Charton (*5*) at 25° C. (7.07×10^{-2} and 3.55×10^{-3}). Apparently, the early work of Ashton and Partington was not accurate.

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Thermochemical Study of the Structures of 1,2-, 2,1-, and 4,1-Nitrosonaphthols

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The heats of combustion and heats of sublimation of 1,2-, 2,4-, and 4,1-nitrosonaphthols were measured. The calculated heats of atomization and heats of combustion (using McGinn's self-consistent set of hydridized bond contributions to heats of combustion) for both the oxime and the nitroso structures were compared with the observed values. The calculations favor the nitroso forms for 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, and 4-nitroso-1-naphthol.

VARIOUS PROPOSALS based on absorption spectra, reduction potentials, and other physical properties have been put forward concerning the molecular structure of the nitrosophenols and the nitrosonaphthols.

Havinga and his associates (*13, 27*) have shown, on the basis of electronic spectra, that *p*-nitrosophenol exists in solution in tautomeric equilibrium with the quinone oxime while only the oxime form exists in the solid state, and that the oxime form of 4-nitroso-1-naphthol is the predominating tautomer in solution. Burawoy and his associates (*6*) have similarly shown that *o*-benzoquinone oxime forms solutions in which the phenolic tautomer prevails, but that 1-nitroso-2-naphthol exists in the oxime form only. Jaffe (*15*) has calculated by the molecular-orbital method that the oxime form of *p*-nitrosophenol should be the more stable.

Hadzi (*12*) investigated the infrared spectra for *p*-nitrosophenol and 4,1-, 2,1-, and 1,2-nitrosonaphthols and found that the oxime formulation correctly represents the structure of these compounds in the solid state, and predominates in their chloroform solutions. However, 2,1-nitrosonaphthol seems to exist in the chelated nitrosoform in solution in carbon tetrachloride. Amstutz, Hunsberger, and Chessick (*1*) found that 1-nitroso-2-naphthol does not show any normal OH vibration and attributed this to chelation of the compound.

On the other hand, Baltazzi (*2*) concluded from his infrared spectral studies that 4,1-nitrosonaphthol is actually a phenol and that the 1,2- and 2,1-nitrosonaphthols are oximes. His conclusions are based on a comparison of the spectra of the alcoholic solutions of 1,2-, 2,1-, and 4,1-nitrosonaphthols with those of their corresponding methyl oxime ethers and their acyl substitution compounds.

The dipole moment studies of Lutskiĭ and Kochergina (*21*) provide evidence for the presence of an intramolecular hydrogen bond in 1,2- and 2,1-nitronaphthols and its absence from 1,2- and 2,1-nitrosonaphthols, and indicate that in benzene 4,1-nitrosonaphthol has mainly a phenolic structure and that 1,2- and 2,1-nitrosonaphthols in benzene and in dioxane have a similar structure.

Because of the widely differing conclusions cited above, additional evidence as to the structures of these compounds, particularly in the solid state, is needed.

EXPERIMENTAL

Materials. Benzoic acid, National Bureau of Standards sample 39h.

Oxygen. Air Reduction Corp. certified pure oxygen was tested for the presence of combustible impurities and carbon dioxide by firing the bomb filled only with 30 atm. of oxygen and analyzing the bomb gases for carbon dioxide, using an analytical train packed as suggested by Prosen and Rossini (*26*). Four analyses indicated that no hydrocarbons or carbon dioxide were present. The magnitude of the error was so small that it would result in an error of less than 0.1% in the determination of carbon dioxide produced by burning 0.5 gram of standard benzoic acid.

1-Nitroso-2-naphthol was synthesized according to the procedure described by Vogel (*29*). The purification procedure was basically that reported by Ilinski (*14*) and was repeated four times before combustion. The resulting pure material had a melting point range of 106.6° to 107.0° C. Analysis (*3*). C, 69.28%; H, 4.15%; N, 8.29%; 0,18.57%.

2-Nitroso-1-naphthol obtained from Eastman Chemical Products, Inc., was recrystallized from distilled water six times and dried in a vacuum desiccator over P_2O_5 before combustion. The purified sample had a melting point range of 144.3° to 145.1° C. Analysis (*3*). C, 69.57%; H, 4.12%; N, 7.91%; O, 18.31%.

4-Nitroso-1-naphthol purchased from K and K Laboratories was recrystallized seven times from benzene. The purified material melted with decomposition at 190° C. Analysis (*11*). C, 69.23%; H, 3.99%; N, 7.96%; O, 18.26%.

To prevent possible contamination of the sample by decomposition products, all calorimetric measurements were made within one week after purification. Each determination reported was made on separately recrystallized fractions.

APPARATUS AND PROCEDURE

The thermochemical measurements were made using a Parr adiabatic oxygen bomb calorimeter with appropriate modifications to make its outer jacket a constant temperature bath.

The temperature changes were measured with a platinum resistance thermometer, calibrated and certified by the National Bureau of Standards, used in conjunction with a G-2 Mueller bridge and a high sensitivity galvanometer. Temperature difference was measured over a range of 1° to 2° C. with a precision of ±0.0005° C.

The corrected temperature rise (ΔR_c), expressed as the increase in resistance in ohms of the given platinum thermometer, was determined graphically according to the method of Dickinson (*10*).

The products of combustion were examined to determine the amount of carbon dioxide formed in the combustion reaction and the amount of nitric acid formed by oxidation of some of the nitrogen. The analytical train used for determining the carbon dioxide was packed as suggested by Prosen and Rossini (*26*). However, the heated furnace was omitted, since only the carbon dioxide formed in the combustion reaction was determined. If combustion was incomplete, the data were not used.

The small amount of nitric acid formed (1 ml. of water was placed in the bomb before combustion) was determined after removal of the gaseous products of combustion by titration with 0.0724*N* sodium carbonate (milliliters of Na_2CO_3 = calories released), using modified methyl orange indicator. The value used for the heat of formation of nitric acid was 57.8 kilojoules per mole.

Heats of sublimation of the three nitrosonaphthols were determined by the Knudsen effusion method. The Knudsen cell, about 1 cm. in diameter and 3 cm. high, was constructed from copper tubing plated with a 50% lead–50% tin alloy. The screw cap contained a window of platinum in which was bored a hole approximately 0.6 mm. in diameter. The cell was placed in a lead well formed in the bottom of a glass tube which was maintained at a constant temperature (±0.01° C.) by immersion in the vapors of refluxing solvent. About 0.2 gram of the compound was placed in the effusion cell and the cap sealed with Teflon tape. The loss in weight of the sample by effusion was determined over a measured period of time, varying from 2 hours and 45 minutes to 5 hours, depending upon the compound. The time necessary to build up maximum vacuum (10^{-5} mm. of Hg or better) was rendered negligible by the length of the run. Three measurements of the effusion rate were made on each compound at each temperature. The apparatus was checked by measuring the heat of sublimation of benzoic acid.

CALIBRATION

The energy equivalent of the calorimeter (E_s) was determined by burning National Bureau of Standards sample 39h benzoic acid with a reported heat of combustion ($-\Delta E_b$) of 26,434 ± 3 joules per gram mass under the conditions of the standard bomb process at 25° C. This value converted to the bomb conditions (final temperature of 29° C.) used during standardization was 26,427.2 joules per gram. To evaluate the energy equivalent of the standard calorimeter, E_s, the following relationship was used:

$$E_s = [(-\Delta E_b(29^\circ\,\text{C.})m_s + q_i + q_n)/\Delta R_c] - \Delta e_1 \text{ joules/ohm} \qquad (1)$$

where

m_s = weight of benzoic acid converted to weight in a vacuum

q_i = mass of nickel alloy fuse wire burned times heat of combustion of fuse wire, 5.86 joules/mg.

q_n = energy released by combustion of N_2 to HNO_3(aq.)

ΔR_c = corrected temperature rise determined graphically

Δe_1 = deviation of energy equivalent from that of standard calorimeter system

Δe_1 was calculated by multiplying the difference in the heat capacity of the benzoic acid pellet and the oxygen it displaced in the filled bomb by 9.931 degrees per ohm, the reciprocal of the temperature coefficient of the platinum resistance thermometer.

The mean result of six successful experiments gave for E_s a value of −102,106.5 joules per ohm with a standard deviation of ±11.3 joules per ohm (Table IA).

RESULTS AND CALCULATIONS

The data are referred to a standard temperature of 25° C. and a pressure of 1 atm. The energy unit used is the calorie, defined as equal to 4.1840 absolute joules.

The quantities m_s, q_i, and q_n were calculated as in the standardization experiments. An additional correction, Δe_2, was calculated in the same manner as Δe_1. Densities of the compounds, determined from the mass and volume of the cylindrical pellets, were 1.11, 1.14, and 1.08 grams per cc. for the 1,2-, 2,1-, and 4,1-nitrosonaphthols, respectively. Heat capacities of the solid compounds estimated from known values for compounds similar in character, molecular weight, and functional groups were 1.14, 1.11, and 1.11 joules per gram for the 1,2-, 2,1-, and 4,1-nitrosonaphthols, respectively.

The quantity of heat observed during the combustion process, *Q* (29°), was calculated from the equation

$$Q = (E_s + \Delta e_2)\Delta R_c \qquad (2)$$

The heat evolved per gram of substance burned in the constant volume bomb process, ΔE_b, was obtained from the relationship

$$-\Delta E_b\,(29^\circ) = (Q - q_i - q_n)/m_s \qquad (3)$$

The term $-\Delta E_b$ was converted to ΔE_c°, the decrease in internal energy for the ideal reaction at 29°, with all reactants and products in their standard states. The difference

Table I. Heat of Combustion Data[a]

A. Standardization with Benzoic Acid

M_s, G.	ΔR_c, Ohms	q_i, Joules	q_n, Joules	e_1, Joules/Ohm	$-E_s$, Joules/Ohm	% Combustion	Av. E_s, Joules/Ohm (Based on 6 Expts.)
0.50430	0.13126	74.5	1.00	5.94	102,101.4	100.06	−102,106.5 ± 11.3

B. Compounds, $C_{10}H_7O_2N$; Mol. Wt. 173.174

Sample	M_s, G.	Δe_2, Joules Ohm	ΔR_c, Ohms	q_i, Joules	q_nJoules	$-\Delta E_{b\ 29^\circ C.}$ Joules/G.	$-\Delta E_c^\circ(29^\circ C.)$, Kcal./Mole	% Combustion
1-Nitroso-2-naphthol	0.47201	5.21	0.13136	69.8	21.2	28,224.8	1167.416	99.9
2-Nitroso-1-naphthol	0.47208	5.08	0.13110	75.8	23.2	28,147.3	1164.207	100.1
4-Nitroso-1-naphthol	0.473083	5.09	0.12995	53.4	21.4	27,890.7	1,153.592	99.9

	No. of Measurements	Av. $-\Delta E_c^\circ(29^\circ C.)$, Kcal./Mole	Av. $\Delta H_c^\circ(298.16^\circ K.)$, Kcal./Mole
1-Nitroso-2-naphthol	5	1167.300 ± 0.218	−1167.53 ± 0.26
2-Nitroso-1-naphthol	5	1164.595 ± 0.505	−1164.83 ± 0.54
4-Nitroso-1-naphthol	5	1153.612 ± 0.256	−1153.85 ± 0.29

[a] In addition to reporting average values, complete data are given for one experiment on each compound.

in energy, $\Delta E_c^\circ - \Delta E_b$, is the Washburn correction and was calculated from formulas given by Prosen (*25*) for groups of experiments in which the masses of compounds used differed by less than 1% from each other.

Calculation of heat of combustion, ΔH_c°, at 29° C. from ΔE_c° involved a term for ΔnRT. For conversion to ΔH_c° at 25° C., heat capacity values other than those of the compounds studied were obtained from the JANAF bulletin (*16*).

The results of the combustion experiments as well as the derived standard heats of combustion are reported in Table IB. The over-all uncertainty assigned to each final value of the heat of combustion was taken as the square root of the sum of the squares of the standard deviation from the mean.

The heats of sublimation (Table II) were calculated using the data obtained from the Knudsen apparatus and a combined form of the Clausius-Clapeyron equation.

$$\log (P_2/P_1) = \log [\text{rate}_{T_2}\ (T_2)^{1/2}]/\text{rate}_{T_1}\ (T_1)^{1/2} = \Delta H_{\text{subl}}/2.303R\ [(T_2 - T_1)/T_2T_1] \qquad (4)$$

A value of 19.9 ± 1 kcal. per mole at 64.0° to 100.0° C. was obtained for benzoic acid and compares favorably with the value of 19.60 kcal. per mole at room temperature reported by Sutter (*28*) from measurements with a highly pressure-sensitive thermistor manometer. The error indicated is only an estimate of the probable error. The precision of reproducing the heat of sublimation was much better than that indicated. The narrow range of pressures over which this method is applicable leads to the conservative estimate of precision given.

Heats of formation of the gaseous compounds from the elements in their standard states (Table II) were derived from the heats of combustion, heats of sublimation, and heats of formation of the combustion products. Values for the standard heats of formation of H_2O (l), −68.3174 kcal. per mole, and CO_2 (g), −94.0518 kcal. per mole, were taken from the National Bureau of Standards (*23*).

Heats of formation of the compounds from gaseous atoms (the negative of their heats of atomization, $-\Delta H_a$) were calculated from the standard heats of formation of the compound, and the heats of dissociation of the elements in their standard state into gaseous atoms (Table II). The values used were ΔH_{subl} (graphite) = 171.7 kcal. per mole (*23*); $\Delta H_a(H_2)$ = 52.09 kcal. (*9*); $\Delta H_a(O_2)$ = 59.16 kcal. (*9*); and $\Delta H_a(N_2)$ = 112.9 kcal. (*9*).

DISCUSSION

In the following discussion an attempt is made to postulate the structures of the three nitrosonaphthols on the basis of the thermodynamic data that have been given.

The heats of atomization, ΔH_a, of the 1,2-, 2,1-, and 4,1-nitrosonaphthols were calculated on the basis of the nitroso structure and of the quinone monoxime and compared with the values derived from our experimental data.

The calculated values of ΔH_a on the basis of the nitroso structure were determined as follows:

$$\Delta H_a \text{ (nitrosonaphthol)} = \Delta H_a \text{ (1- or 2-naphthol)} - \text{(C—H bond energy term)} + \text{(C—N term)} + \text{(N = O term)}$$

The values of ΔH_a for 1- and 2-naphthols were determined from their respective heats of combustion, −1186.9 and −1184.0 kcal. (*20*), and their heats of sublimation as calculated from the Clausius-Clapeyron equation using values given by Jordan (*17*) for their vapor pressures at various temperatures. To make these calculations, a minimum number of bond energy terms were used (Table III).

Table IVA compares the calculated values of ΔH_a for the nitroso and quinone monoxime structures with the values derived from our experimental data.

In the case of the quinone monoxime structure the total bond energies of the nitrosonaphthols were calculated as follows:

$$\Delta H_a \text{ (quinone monoxime structure)} = \Delta H_a \text{ (1,2- or 1,4-naphthoquinone)} - (\text{—C=O}) + (\text{—C=N}) + (\text{—N=O}) + (\text{—O—H})$$

The heats of atomization of 1,2- and 1,4-naphthoquinones were calculated from their respective heats of combustion (−1110.3 and −1103.7 kcal.) (*18*) and their heats of sublimation, which were estimated from the value of compounds similar in structure (17.0 kcal.).

To substantiate further the structures of the nitrosonaphthols, their experimentally determined heats of combustion, ΔH_c, were compared with those calculated from a self-consistent set of bond energy terms.

McGinn (*22*) has calculated the contribution to the heat of combustion for some hybrid carbon bonds, using the principle of Noller (*24*). Employing the values calculated by McGinn (Table V), the heats of combustion of the nitrosonaphthols were calculated.

Table II. Heats of Sublimation, Formation, and Atomization

Compound	Heat of Sublimation, Kcal.	Heat of Formation (Gas), Kcal.	Heat of Atomization, Kcal.
1-Nitroso-2-naphthol	20.7 ± 1	8.60	2304.3
2-Nitroso-1-naphthol	13.5 ± 1	−1.30	2314.2
4-Nitroso-1-naphthol	20.9 ± 1	−4.88	2317.7

Table III. Bond Energy Terms and Their Source

	Kcal./Mole	
E(C—H)	98.9	(*7*)
E(C—N)	73	(*7, 8*)
E(C=O)	179.3	(*8*)
E(C=N)	147	(*8, 9*)
E(N—O)	53	(*9*)
E(N=O)	134	(*5, 9*)
E(O—H)	110.6	(*9*)

Table IV. Experimental and Calculated ΔH_a and ΔH_c Values

A. Summary of ΔH_a Values

Compound	ΔH_a(exptl.), Kcal./Mole	ΔH_a(Calcd. for Nitroso), Kcal./Mole	ΔH_a(Calcd. for Quinone), Kcal./Mole
2-Nitroso-1-naphthol	2314.2	2316.0	2297.3
4-Nitroso-1-naphthol	2317.7	2316.0	2303.9
1-Nitroso-2-naphthol	2304.3	2307.5	2297.3

B. ΔH_c (for Gaseous Molecules at 25° C.)

	ΔH_c(obsd.), Kcal./Mole	ΔH_c(Calcd. for Nitroso), Kcal./Mole	ΔH_c(Calcd. for Quinone), Kcal./Mole
2-Nitroso-1-naphthol	1178.3	1174.0	1142.1
4-Nitroso-1-naphthol	1174.7	1174.0	1135.5
1-Nitroso-2-naphthol	1188.2	1172.0	1142.1

To calculate ΔH_c of the nitrosonaphthols assuming the nitroso structure, it was necessary to obtain the contribution to ΔH_c of the C—O—H and the C—N=O groups. In the following calculations all heats of combustion are given for the gaseous molecule at 25° C. The heats of combustion used are listed in Table VI. The contribution to ΔH_c for the C—O—H group was determined as follows:

$$\Delta H_c \text{ (1- or 2-naphthol)} - [\Delta H_c\text{(naphthalene)} - \mathrm{HC}_{sp}2_{\pi}2] = \text{C—O—H contribution} \qquad (5)$$

For 1-naphthol the C—O—H contribution is −5.2 kcal; for 2-naphthol, −7.2 kcal. The contribution to ΔH_c for the C—N=O group is given by:

$$\Delta H_c\text{(nitrosobenzene)} - [\Delta H_c\text{(benzene)} - \mathrm{HC}_{sp}2_{\pi}2] = \text{C—N=O} = 15.0 \text{ kcal.} \qquad (6)$$

A consideration of the three nitrosonaphthols shows that the molecules consist of six $C_{sp}2_{\pi}2$, four $C_{sp}2_{\pi}2 - C_{sp}2_{\pi}3$, one $C_{sp}2_{\pi}3 - C_{sp}2_{\pi}3$, and six $HC_{sp}2_{\pi}2$ bonds, as well as one C—O—H group and one C—N=O group.

Table IVB compares the calculated and experimentally determined heats of combustion. To make the calculations assuming the quinone monoxime structure, it was necessary to obtain the contribution to ΔH_c for two $C_{sp}2_{\pi}2 - C_{sp}2_{\pi}2$ and three $C_{sp}2_{\pi} - C_{sp}2_{\pi}$ bonds plus one C=O group and one C=N—O—H group. In addition, the contribution to ΔH_c for the $HC_{sp}3$ bond was necessary in order to calculate the C=N—O—H group contribution. The contributions for the various groups were calculated as follows:

For $HC_{sp}3$:

$$\tfrac{1}{3}\,[\Delta H_c\text{(toluene)} - (C_{sp}3 - C_{sp}2_{\pi}2) - \{\Delta H_c\text{(benzene)} - \mathrm{HC}_{sp}2_{\pi}2\}] = \mathrm{HC}_{sp}3 \text{ bond contribution} = 52.6 \text{ kcal.} \qquad (7)$$

Table V. Contribution to Heat of Combustion for Some Hybrid Carbon Bonds (9)

(Values for gaseous molecule at 25° C.)

	Kcal./Mole
$HC_{sp}2_{\pi}2$	42.73
$C_{sp}3 - C_{sp}2_{\pi}2$	39.43
$C_{sp}2_{\pi}2 - C_{sp}2_{\pi}2$	88.84
$C_{sp}2_{\pi}2 - C_{sp}2_{\pi}3$	77.72
$C_{sp}2_{\pi}3 - C_{sp}2_{\pi}3$	63.93
$C=O$	62.5

Table VI. Heats of Combustion of Gaseous Molecules at 25° C. and Their Source

	Kcal.
Nitrosobenzene	761.4 (*19*)
Naphthalene	1249.7 (*22*)
Benzene	789.1 (*22*)
Toluene	943.6 (*22*)
Cyclohexanedione-dioxime	889.3 (*4*)
Cyclohexane	945.2 (*18*)

For the C=N—O—H group:

$$\tfrac{1}{2}[\Delta H_c\text{(cyclohexanedione-dioxime)} - \{\Delta H_c\text{(cyclohexane)} - 4\ \mathrm{HC}_{sp}3\}] = \text{C=N—O—H contribution} = 77.25 \text{ kcal.} \qquad (8)$$

The contributions for the two $C_{sp}2_{\pi}2 - C_{sp}2_{\pi}2$ and the three $C_{sp}2_{\pi} - C_{sp}2_{\pi}$ bonds, as well as that for the C=O group, can be determined together as follows:

$$\Delta H_c\text{(naphthoquinone)} - [\Delta H_c\text{(naphthalene)} - 2(\mathrm{HC}_{sp}2_{\pi}2) - 4(C_{sp}2_{\pi}2 - C_{sp}2_{\pi}3) - (C_{sp}2_{\pi}3 - C_{sp}2_{\pi}3)] - \text{C=O group} = \text{total contribution} \qquad (9)$$

Using 1,2-naphthoquinone: total contribution = 275.4 kcal. Using 1,4-naphthoquinone: total contribution = 268.8 kcal. The value used for the C=O group contribution to the heat of combustion was that given by Franklin (*30*).

SUMMARY AND CONCLUSIONS

A comparison of the calculated ΔH_a and ΔH_c values with those derived from our experimental data (Table IV) gives good evidence that 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, and 4-nitroso-1-naphthal all exist in the nitroso form.

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Solute Activity Coefficients at Infinite Dilution via Gas-Liquid Chromatography

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Gas-Liquid chromatographic specific retention volumes and solute activity coefficients at infinite dilution in the liquid phase have been measured for 10 nonpolar binary systems (methane through *n*-decane in *n*-hexadecane) and five systems (benzene through *n*-butylbenzene in *n*-hexadecane) with aromatic solutes and nonpolar substrate. All systems were measured at 40°, 70°, and 90° C. All of the solutes are volatile (vapor pressures of pure substances greater than 30 mm. of Hg in all but four cases) while the solvent was nonvolatile (vapor pressure less than 0.4 mm. of Hg) at all operating temperatures. The results allow interpolation of the activity coefficients of *n*-undecane through *n*-pentadecane on the three isotherms.

ACTIVITY coefficients determined in this work by gas-liquid chromatography (GLC) were found to agree well in the cases where comparison with those extrapolated from static measurements in the bulk liquid at well-defined equilibrium conditions were available (*2, 7, 14*). Other workers have found the same result for other systems (*4, 8, 11*).

The following expression developed by Martire (*9*) relates the solute activity coefficient at infinite dilution in the liquid phase (γ_b^∞) to the GLC measured specific retention volume (V_g):

$$\gamma_b^\infty = \frac{RT}{M_a p_b^0 V_g} \qquad (1)$$

This relation can be developed using the definitions of the partition coefficient given by Kaiser (*6*) and Burchfield (*3*). Martire (*10*) and Martire and Pollara (*13*) give the following assumptions, implicit and explicit, as being basic in the derivation of Equation 1: both the vapor of the pure solute and the vapor phase above the solution behave ideally; and with the pure solute as the standard state and if x_b is solute mole fraction, then $x_b \to 1$, $\gamma_b \to 1$.

The meaning of the specific corrected retention volume is discussed in detail by Littlewood, Phillips, and Price (*8*). To paraphrase (*8*): under constant experimental conditions, the peak maximum for a particular vapor will appear at a characteristic time. This time, the retention time, is a function of the nature of the vapor, the stationary phase, and the column temperature. It is also dependent on experimental parameters such as the gas-flow rate, the dead volume, and the weight of stationary phase. Thus the retention volume V_r must be corrected to eliminate the effects of the experimental parameters. This is accomplished through the use of Equation 2.

EXPERIMENTAL

The experimental procedure was essentially the same as that used by other workers (*7, 10, 11, 13*). Only procedural and equipment differences will be discussed here.

The column was made from ⅛-inch O.D. copper tubing. The packing consisted of a 19.8% by weight stationary liquid phase of *n*-hexadecane on a solid support of 40- to 60-mesh C-22 Firebrick. The column was installed in a Wilkens Aerograph Hi-Fy Model 600-B equipped with a flame ionization detector. Column temperature was measured at six points with copper-constantan thermocouples, and the oven temperature was further monitored by use of a Beckman thermometer.

At thermal equilibrium, oven temperature was maintained to within ±0.3° C. during the course of the day and ±0.1° C. during short measurement periods. Carrier gas (nitrogen) flow rate was measured with a soap-film meter in conjunction with a Heuer stop watch. This watch was 10 seconds full scale and with divisions of 0.1 second. This unit was also used in measuring retention times for the calculation of the retention volume, V_r. The inlet pressure was controlled and measured to within ±3 mm. of Hg by a needle valve and calibrated pressure gauge. The column outlet pressure was always atmospheric. Blended liquid samples

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