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Henry's Law Constants of Carbonyl−Pentafluorobenzyl Hydroxylamine (PFBHA) Derivatives in Aqueous Solution

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In situ derivatization of airborne carbonyls can increase the efficiency of sampling methods aimed at the quantification of these trace components in urban and rural atmospheres. The design of efficient samplers based on aqueous solutions of the derivatization reagent *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) requires knowledge of how the carbonyl−PFBHA derivatives partition between water and air. We have determined the Henry's law constant at 25 °C for 16 PFBHA derivatives of carbonyls that represent typical analytes present in the ambient environment. The inert gas stripping method was employed, followed by measurement of the aqueous concentration of the derivatives by GC−ion trap mass spectrometry (GC/ITMS). The values of the Henry's law constants ranged from (37 to 268) Pa·m^3·mol^{-1}. We evaluated several molecular descriptors to investigate quantitative structure−property relationships (QSPRs) for the partition behavior of these compounds. The molecular volume, the molecular surface area, and the polarizability correlate better with k_H, while the dipole moment proved to be an extremely insensitive descriptor. The temperature dependence of k_H in the range (5 to 25) °C was evaluated. These data led to the estimation of ΔH^∞ and ΔS^∞, which ranged from ΔH^∞ = (17 to 60) kJ·mol^{-1} and ΔS^∞ = (36 to 170) J·K^{-1}·mol^{-1}.

Introduction

O-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine (PFBHA) is a popular derivatization reagent for trace organic analysis of carbonyls.[1−7] The product of the reaction is an oxime which is thermally stable and insensitive to light.[4,8] Applications of PFBHA derivatization include the analysis of airborne carbonyls emitted into the atmosphere by anthropogenic and biogenic sources,[4−7,9,10] the analysis of polar organic byproducts of drinking water disinfection with ozone,[11−14] and the study of carbonyls generated by lipid peroxidation and other biological processes.[15,16]

The employment of PFBHA derivatization improves the sensitivity and resolution of gas chromatography methods toward carbonyls.[6] The advantages of this method compared with the classical 2,4-dinitrophenylhydrazine (DNPH) derivatization are (1) higher stability of the α,β-unsaturated carbonyl (e.g., acrolein, crotonaldehyde) and dicarbonyl (e.g., glyoxal, methylglyoxal) derivatives;[17,18] (2) the ability to distinguish α-dicarbonyls from hydroxycarbonyls; and (3) the ability to obtain unambiguous molecular weight determinations by interpretation of the electron ionization (EI), methane chemical ionization (CH_4-CI), and pentafluorobenzyl alcohol chemical ionization (PFBOH-CI) ion trap mass spectra.[1,3,6]

In situ PFBHA derivatization has been implemented in the collection of airborne carbonyls by sampling with water-based techniques such as impingers and mist chambers,[1,19] and also in methods that utilize solid sorbents.[20−23] An important reason for developing sampling procedures with *in situ* PFBHA derivatization is to stabilize labile or reactive carbonyls, which in some cases cannot be preserved in stainless steel canisters[24,25] or dissolved in water, both in its underivatized form[26] and by DNPH derivatization.[17,18] In previous work, we observed a relationship between the k_H values of free carbonyls and the collection efficiency in sampling devices that rely on partitioning of the carbonyls to aqueous solutions (e.g., impingers and mist chambers).[1] While the partitioning of the solutes from the gas to the aqueous phase is an important process that affects the collection efficiency, several other processes also should be considered, such as the hydration and formation of gem-diols, the possible decomposition of labile analytes and their hydrates in water, PFBHA derivatization rates, and evaporative loss of free and derivatized carbonyls. In Figure 1, we illustrate these processes at the liquid−air interface. The extent of evaporation of free carbonyls can be estimated from Henry's law constants for these compounds that are readily available in the literature.[27−34] However, no information exists regarding the Henry's law constants of the PFBHA derivatives. The objective of this

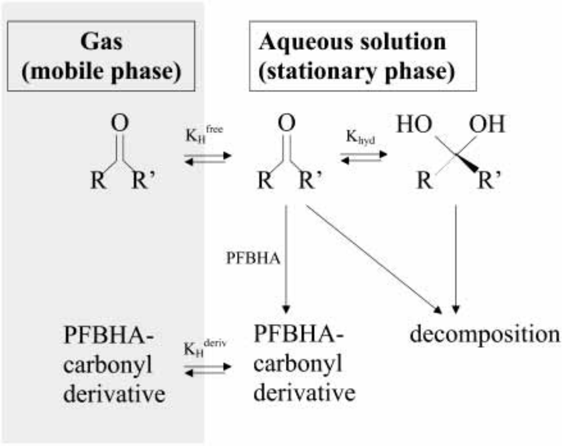

Figure 1. Chemical reactions taking place in solution and partition of the solutes to the gas phase during sampling with *in situ* derivatization.

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work is to provide experimental information on the k_H of carbonyl−PFBHA derivatives that can be used to gain insight into processes affecting the collection efficiency of sampling devices that rely on dissolution of gas-phase analytes.

The Henry's law constant (k_H) is a thermodynamic parameter that plays a fundamental role in the description of many industrial, toxicological, and environmental processes that transport chemicals between gaseous and aqueous phases. It is defined as

$$k_H = \lim_{x_2 \to 0} \frac{f_2}{x_2} \tag{1}$$

where f_2 is the solute fugacity and x_2 is the solute mole fraction in the liquid solution.[35] For dilute ($x_2 < 10^{-3}$) and low-volatility organic solutes, the Henry's law constant is often expressed as the ratio of the equilibrium partial pressure of the solute (p_g, expressed in Pa) divided by its aqueous concentration (C_w, expressed in $\text{mol}\cdot\text{m}^{-3}$).

$$k_H = \frac{p_g}{C_w} \tag{2}$$

The dimensionless Henry's law constant (air−water partition coefficient, k_{aw}) is related to the k_H through the ideal gas law, as follows:

$$k_{aw} = \frac{k_H}{RT} = \frac{C_g}{C_w} \tag{3}$$

The k_H can be estimated in some cases as the ratio of the solute's standard vapor pressure and its aqueous solubility at 25 °C.[36] This approach is limited to solutes that present very low solubility in water and for which precise measurements of both quantities are available. The latter is not the case in the present work.

The temperature dependence of k_{aw} (or k_H) is expressed by the Gibbs−Helmholz equation:

$$-RT \ln k_{aw} = \Delta H^{\infty} - T\Delta S^{\infty} \tag{4}$$

where ΔH^{∞} and ΔS^{∞} are the molar enthalpy change and the entropy variation corresponding to the dissolution of a gaseous solute at infinite dilution, respectively. An estimation of these parameters can be obtained by determining k_H at various temperatures, assuming that ΔH^{∞} and ΔS^{∞} are independent of temperature (a reasonable assumption over small temperature ranges).

In the present study, we report the experimental determination of Henry's law constants (in the range 37 to 268 $\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$) corresponding to 16 carbonyl−PFBHA derivatives, and the temperature dependence study for 8 of those, for temperature ranging from (5 to 25) °C. The carbonyls investigated represent typical analytes observed in urban atmospheric sample extracts, such as aliphatic saturated C_1−C_{10} carbonyls (formaldehyde, acetaldehyde, acetone, 2-butanone, 2-pentanone, hexanal, octanal, and decanal), aliphatic unsaturated carbonyls (acrolein and crotonaldehyde), monoaromatic carbonyls (benzaldehyde and *p*-tolualdehyde), oxygenated polyaromatic hydrocarbons (9-fluorenone), dicarbonyls (glyoxal), and hydroxycarbonyls (hydroxyacetone and 3-hydroxy-3-methyl-2-butanone).

Experimental Section

Reagents. Authentic standards for formaldehyde, acetaldehyde, acetone, 2-butanone, 2-pentanone, hexanal, octanal, decanal, acrolein, crotonaldehyde, *p*-tolualdehyde, fluorenone, glyoxal, hydroxyacetone, and 3-hydroxy-3-methyl-2-butanone, were purchased from Aldrich Chemical Co. (Milwaukee, WI); benzaldehyde was purchased from Acros Organics (New Jersey). These standards were utilized without further purification. *O*-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine was purchased from Aldrich (Milwaukee, WI) and further purified by recrystallizing two times in distilled isopropyl alcohol (Fisher Scientific, Pittsburgh, PA). High-purity HPLC quality dichloromethane was purchased from Burdick and Jackson (Muskegon, MI) and distilled. The HPLC grade water (Fisher Scientific, Pittsburgh, PA) employed in the sampling was distilled over $KMnO_4$ to oxidize the organics in the water. The glassware was silanized by immersion in a 15 vol % solution of dichlorodimethylsilane in toluene to minimize analyte adsorption to the container walls.

Determination of Henry's Law Constant. We determined the k_H by the inert gas stripping (IGS) method, developed by Mackay et al.[37−39] A flow of N_2(g) was introduced in the bottom of a column containing an aqueous solution of the analytes and was dispersed in small bubbles at a known and constant flow rate. The gas flowed through the well-mixed aqueous solution column, ensuring that the gas exiting the column was in equilibrium with the liquid. By measuring the decrease of the solute concentration in water, k_H can be calculated from a simple mass balance for the solute. During the stripping process, the mass balance for the solute can be expressed in terms of transfer rates from the liquid to the gaseous phase as

$$-V \frac{\partial C_w}{\partial t} = \frac{p_g G}{RT} \tag{5}$$

where V is the volume of the liquid, G is the gas flow rate, R is the gas constant, and T is the temperature of the system. Combining eqs 1 and 2 and integrating from the initial conditions $t = 0$ and $C_w = C_w^{\circ}$ (the initial concentration), the expression

$$\ln\left(\frac{C_w}{C_w^{\circ}}\right) = -\left(\frac{k_H G}{VRT}\right)t \tag{6}$$

can be used to obtain the experimental k_H value from the slope of the linear regression of $\ln(C_w/C_w^{\circ})$ versus time, when all other parameters are fixed.

Preparation of Aqueous Solutions of PFBHA−Carbonyl Derivatives. The derivatization reaction was carried out in an aqueous solution containing a mixture of the studied carbonyls (in the range 50 to 7500 $\mu\text{g mL}^{-1}$, total molar concentration 0.6 mM) and excess PFBHA (5 mM). Each individual carbonyl concentration was lower than the corresponding solubility in water, when that value existed. The solution was kept in the dark at room temperature for 24 h to ensure reaction completion. A 2 L sample was prepared by 1:500 dilution of the original solution with water (HPLC grade, Fisher). The diluted solution (concentration of carbonyls ranging from 0.1 to 15 $\mu\text{g mL}^{-1}$) was employed to determine the k_H (1 L was used in each column experiment). Initial concentrations corresponding to each carbonyl PFBHA derivative are reported in Table 1. In each case, concentrations were lower than the corresponding solubility in water. The experimental uncertainty associated with the initial concentrations was between 3% and 6%.

Experimental Determinations of k_H. The apparatus employed consisted of two glass columns (60 cm height, 51 mm i.d.), which allowed for simultaneous determination

Table 1. k_H Determined at 298 K for 16 Carbonyl−PFBHA Derivatives, Compared with Those Reported for the Free Carbonyls in Aqueous Solution

carbonyl	C_0 $\mu g \cdot mL^{-1}$	k_H(this work) $Pa \cdot m^3 \cdot mol^{-1}$	k_H(free)[a] $Pa \cdot m^3 \cdot mol^{-1}$	ref
Saturated Aliphatic Carbonyls				
formaldehyde	7.07	61.3 ± 6.2	0.030	29
			0.033	27
acetaldehyde	14.1	53.0 ± 4.9	5.88	29
			7.69	30
			9.09	27
acetone	12.3	90.3 ± 5.9	2.86	29
			3.13	28
2-butanone	0.62	215 ± 12	5.00	29
			5.56	30
2-pentanone	0.65	268 ± 41	8.33	34
hexanal	0.49	173 ± 17	20.83	29
octanal	0.19	126 ± 21	50.0	29
decanal	0.21	41 ± 26	163.93	29
Unsaturated Aliphatic Carbonyls				
acrolein	1.62	105.2 ± 4.2	11.1	31
crotonaldehyde	1.18	147 ± 15	1.96	34
Monoaromatic Carbonyls				
benzaldehyde	3.99	199 ± 21	2.38	29
			2.70	27
p-tolualdehyde	0.84	151 ± 28	[0.91][b]	28
Polyaromatic Carbonyls				
9-fluorenone	1.42	91 ± 22	[<7.9][c]	32
Dicarbonyls				
glyoxal	0.55	62 ± 24	$<3.3 \times 10^{-4}$	27
Hydroxycarbonyls				
hydroxyacetone	0.31	37 ± 13	0.0128	33
3-hydroxy-3-methyl-2-butanone	0.095	81 ± 23	n.a.[d]	

[a] k_H for free carbonyl, literature values. [b] Value for the isomer methyl phenyl ketone. [c] Value for 9-H-fluorene. [d] n.a.: no data available.

Table 2. Verification of the Experimental Method's Performance, Based on Known k_H Values of Aromatic Solutes

	C_0 μM	k_H(this work) $Pa \cdot m^3 \cdot mol^{-1}$	k_H(lit.) $Pa \cdot m^3 \cdot mol^{-1}$	% rel diff	ref
toluene	1227	495.0	476.2	3.8	45
			526.3	−6.3	46
			588.2	−18.8	47
			666.7	−34.7	48
naphthalene	132	42.2	41.7	1.2	49
			47.6	−12.8	37
biphenyl	10.1	29.6	27.8	6.1	49
			40.0	−35.1	37

of k_H in two different solutions. External glass cooling jackets were used for circulation of a thermostatic fluid. The columns were silanized internally to minimize analyte adsorption to the column walls. Silanization of the columns was performed by filling them with a 15 vol % solution of dichlorodimethylsilane in toluene. The temperature was controlled by an external bath with heating and refrigerating capabilities (VWR−Polysciences), capable of keeping the system within ±0.1 °C of the set value. The temperature in each column was monitored with digital thermometers calibrated to ±0.1 °C. The gas flow rate was regulated with independent flow controllers in each column, which were calibrated with a soap film flow meter in the range (10 to100) mL/min. Nitrogen gas (99.997% Airgas), injected into the bottom of each column, was previously saturated with water by bubbling into a preconditioning flask. The solutions in each column were stirred with magnetic bars. Samples (1 mL) were withdrawn at a specific time by means of a glass syringe and were stored in amber glass vials with PTFE seals prior to extraction and analysis. The exact mass of each aliquot was determined with an error of ±10 mg (±1%).

To evaluate the experimental approach, we determined the Henry's law constants of three organic solutes for which k_H values were determined previously. The solutes were toluene, naphthalene, and biphenyl. These k_H values expand over an order of magnitude, within the range of k_H values expected for our PFBHA−carbonyl derivatives. Individual solutions were prepared for each solute, and the concentration was determined spectrophotometrically at 25 °C (Hewlett-Packard 8452-A; toluene, $\lambda_{max} = 262$ nm, $\epsilon = 251$ $M^{-1} \cdot cm^{-1}$; naphthalene, $\lambda_{max} = 276$ nm, $\epsilon = 2500$ $M^{-1} \cdot cm^{-1}$; biphenyl, $\lambda_{max} = 250$ nm, $\epsilon = 15850$ $M^{-1} \cdot cm^{-1}$). The experimentally determined k_H values, reported in Table 2 are in good agreement with literature data, which indicates that, under the present experimental conditions, equilibrium between the liquid and gas phases is attained satisfactorily.

Extraction, Isolation, and Gas Chromatography/Mass Spectrometry. The PFBHA−carbonyl derivatives in the samples were extracted in CCl_2H_2 after acidification with H_2SO_4(aq). Residual water in the extract was eliminated by passing the extracts through anhydrous Na_2SO_4(s) columns (8 cm length, 5 mm i.d.). The eluate was collected and reduced to 200 μL by evaporation of the solvent under a mild N_2(g) stream. The extract was split into two (100 μL) aliquots. The PFBHA derivatives in one extract were analyzed by using GC/ion trap mass spectrometry (GC/ITMS). The PFBHA derivatives of carbonyls containing hydroxyl or carboxyl moieties in the second aliquot were silylated by using a 10:1 mixture of BSTFA and trimethylchlorosilane (TMCS, catalyst) and were further analyzed by GC/ITMS.

A Varian Star 3400 CX gas chromatograph interfaced to a Saturn 2000 ion trap mass spectrometer was utilized. The injector was programmed to maintain a temperature of 280 °C during the first minute, and then it was increased to 310 °C at 50 °C/min (splitless injection mode). High-resolution gas chromatographic (HRGC) separation was performed on a 30 m × 0.25 mm (i.d) DB-17 HRGC column with a 0.25 μm film thickness (Agilent Technologies, Folsom, CA). The oven temperature was programmed to maintain a temperature of 70 °C for 1 min. The oven temperature was increased to 100 °C at a rate of 5 °C/min, and then it was increased to 280 °C at a rate of 10 °C/min and to 310 °C at a rate of 30 °C/min. The temperature was maintained at 310 °C/min for 10 min. Methane chemical ionization (CH_4-CI) ion trap mass spectra were obtained with a filament current of 10 μA and an ion trap temperature of 150 °C. Automatic reaction control using a maximum ionization time of 500 μs, a maximum reaction time of 80 ms, and an ion target of 5000 was employed. Methane was introduced into the ion trap until the ratio between the *m*/*z* 17 and *m*/*z* 29 ions was about 1:1. The masses were scanned from 50 to 650 amu.

Identification and Quantification. The approach to identify the carbonyls was described in previous work.[6,19] Briefly, the molecular weight of the carbonyls is determined by the presence of the $(M + H)^+$ ion in the methane CI mass spectra, and identification is based on interpretation of the mass spectrum and matching the relative retention time to that of an authentic standard. The retention times and relative retention times of the PFBHA or PFBHA/BSTFA derivatives studied in this work were previously determined.[19] The $(M + H)^+$ ions of PFBHA and PFBHA/

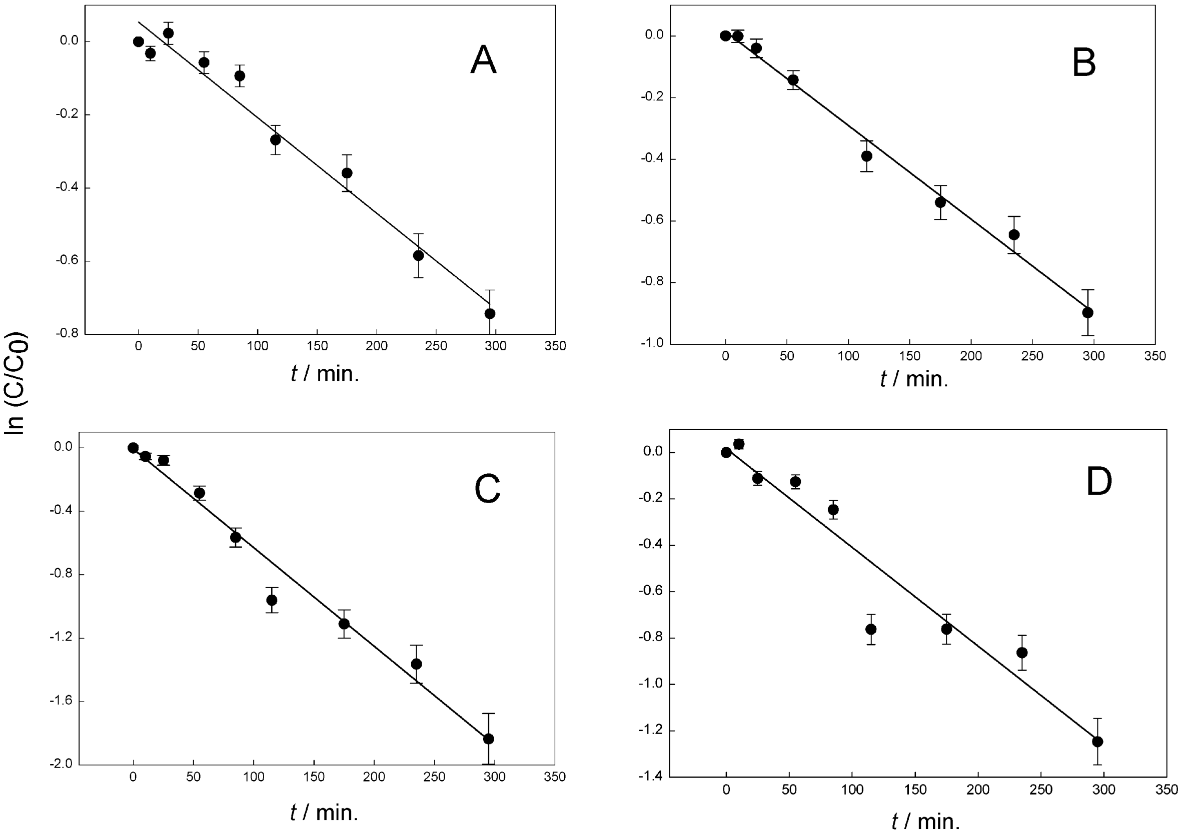

Figure 2. Typical experimental results obtained in the determination of Henry's law constants of carbonyl−PFBHA derivatives. C and C_0 are the actual and initial concentrations of the analyte in the aqueous phase, respectively. A, acetone; B, acrolein; C, 2-butanone; D, crotonaldehyde.

BSTFA derivatives were used for quantification, which was accomplished by internal standardization. A linear calibration curve was constructed for each analyte by plotting the [(peak area of the derivative of the analyte)/(peak area of the derivative of the internal standard)] versus concentration of the analyte in the range (50 to 1000) pg/μL. $^{13}C_3$-acetone (retention time $t_r = 9.65$ min) was employed as the internal standard to quantify saturated and unsaturated aliphatic carbonyls. 4-Fluorobenzaldehyde ($t_r = 17.65$ and 17.77 min) was utilized as the internal standard to quantify aromatic carbonyls and dicarbonyls, and 4-hydroxy-$^{13}C_6$-benzaldehyde ($t_r = 21.61$ min for the PFBHA derivative and 21.78 for the PFBHA−BSTFA derivative) was employed as the internal standard to quantify hydroxycarbonyls.

Results and Discussion

Determination of k_H at 25 °C. To exemplify the results, in Figure 2, we present plots of experimental values obtained in the determination of k_H of the PFBHA derivatives of acetone, acrolein, 2-butanone, and crotonaldehyde, where C is the actual concentration measured at a given stripping time and C_0 is the initial analyte concentration. The individual data errors were within 3−6% in all cases, based on the standard deviation of the slope of chromatographic calibration curves. In Table 1, we report the Henry's law constant values determined for these and the other 12 derivatives corresponding to various types of carbonyls. The k_H values were calculated using eq 6, and they range from (37 to 268) $Pa \cdot m^3 \cdot mol^{-1}$. The experimental errors indicated for each k_H were estimated from the standard deviation of the linear regression equations.

The data corresponding to derivatives of saturated aliphatic carbonyls suggest that k_H increases with the number of C atoms in the carbonyl, reaching a maximum near C_5 (2-pentanone), and further decreases at higher molecular weights. Such behavior indicates that increasing the molecular size of the solute may affect differently its chemical potential in the gaseous and aqueous phases. By replacing the fugacity f_2 in eq 1 with the Raoult's law expression for the vapor pressure $p_g = x_2 p_g^\circ \gamma^\infty$, the Henry's law constant can be expressed as the product of the limiting activity coefficient in water γ^∞ and the vapor pressure of the pure solute p_g° as follows:[35,40]

$$k_H = \gamma^\infty p_g^\circ \tag{7}$$

The magnitude of the limiting activity coefficient γ^∞ is an indication of the deviation of dilute solutes from Raoult's law. In the case of nonelectrolyte organic solutes in water, γ^∞ is usually larger than 1, and for large aromatic solutes of the kind of the studied PFBHA derivatives, it typically ranges between 10^4 and 10^6.[40,41] Thus, γ^∞ is related to the solute's tendency to escape from aqueous solution, and it likely increases with the molecular size of the derivatives. In contrast, the vapor pressure p_g° decreases at higher molecular weight within a homologous series of compounds.[41] Therefore, it is reasonable to assume that a balance between growing γ^∞ and decreasing p_g° is responsible for the overall observed bell-shaped behavior of k_H. Experimental data are not available for γ^∞ and p_g° of the studied solutes, and traditional predictive methods for γ^∞ such as UNIFAC and other group contribution techniques are not precise when applied to large organic solutes in aqueous solution.[40]

Given the large number of chemicals of potential concern, the difficulties of k_H experimental determinations, and

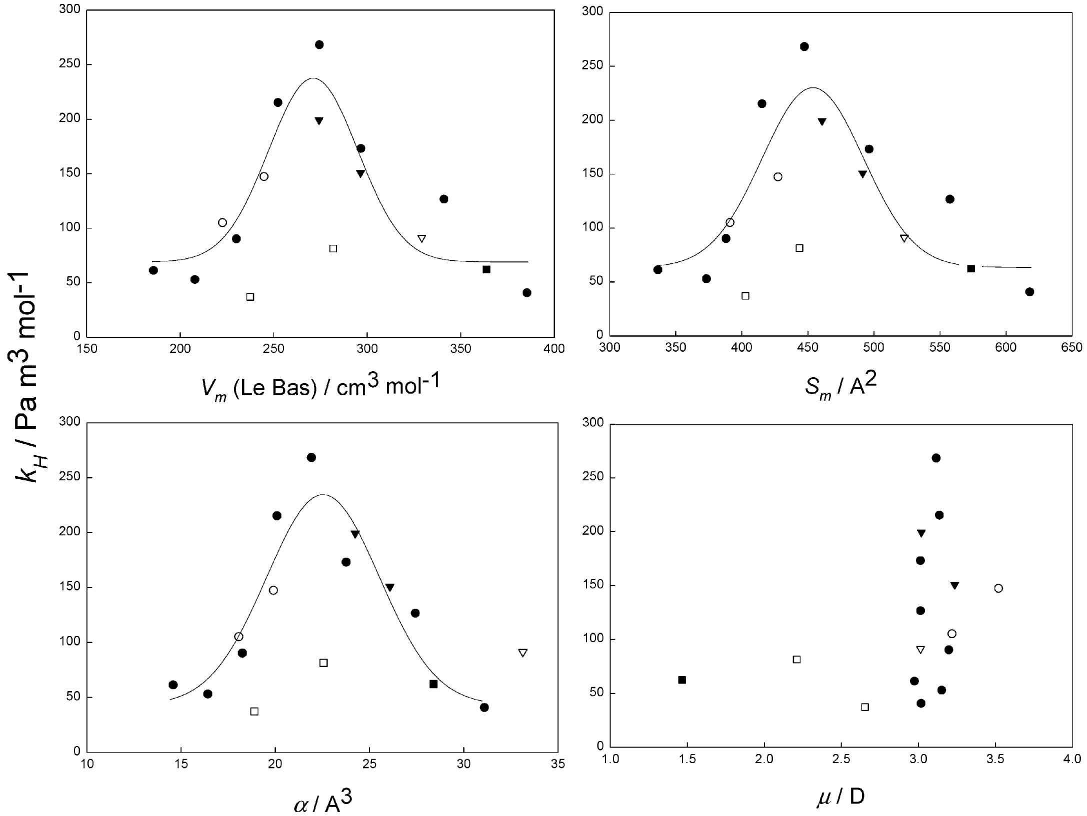

Figure 3. Quantitative structure–property relationships (QSPRs) between the determined k_H values of carbonyl–PFBHA derivatives and the Le Bas molecular volume, V_m(Le Bas), molecular surface area, S_m, polarizability, α, and dipole moment, μ, estimated for the following: ●, aliphatic saturated carbonyls; ○, aliphatic unsaturated carbonyls; ▼, monoaromatic carbonyls; ▽, oxy-PAH; ■, dicarbonyls; □, hydroxycarbonyls. The curves represent the data fit with eq 8.

Table 3. Molecular Descriptors of Model Compounds

	μ	α	S_m	V_m	V_m(Le Bas)
	D	Å^3	Å^2	Å^3	cm^3·mol^{-1}
formaldehyde	2.974	14.58	336	505	185.6
acetaldehyde	3.151	16.42	373	562	207.8
acetone	3.198	18.25	388	600	230.0
2-butanone	3.136	20.09	415	653	252.2
2-pentanone	3.115	21.92	447	705	274.4
hexanal	3.013	23.76	496	775	296.6
octanal	3.014	27.43	557	883	341.0
decanal	3.018	31.10	618	990	385.4
acrolein	3.218	18.06	391	599	222.6
crotonaldehyde	3.525	19.90	427	654	244.8
benzaldehyde	3.019	24.24	461	726	274.2
p-tolualdehyde	3.235	26.08	491	778	296.4
9-fluorenone	3.014	33.13	523	877	329.1
glyoxal	1.466	28.39	573	907	363.8
hydroxyacetone	2.653	18.89	403	623	237.4
3-hydroxy-3-methyl-2-butanone	2.211	22.56	443	717	281.8

Table 4. Fitting Parameters for Eq 8

X	*a*	*b*	*c*	*d*
V_m	69.1	168.5	271	23.9
S_m	63.6	166.6	453.8	38.4
α	43.2	191.4	22.5	2.99

scientific interest in elucidating the fundamental molecular determinants of physical–chemical properties, a considerable effort has been devoted to generating quantitative structure–activity (or structure–property) relationships (QSARs/QSPRs).[41,42] In the present study, we correlate the experimental k_H values with several molecular descriptors for solute–solvent and solute–solute interactions, such as the solute molecular surface area (S_m), the molecular volume (V_m), its dipole moment (μ), and polarizability (α). The values employed for these descriptors are presented in Table 3. We computed these properties by performing AM1 semiempirical quantum chemistry calculations of the 16 PFBHA–carbonyl derivatives with the Hyperchem software package.[43,44] The geometry of each derivative in the vacuum was fully optimized without symmetry constraints, performing restricted RHF calculations. The molecular volume was also estimated by the classical Le Bas method, which is based on the summation of atomic volumes with adjustments for ring formation and other contractions due to specific bonds.[41] In Figure 3, the correlation between k_H and these descriptors is presented (only the Le Bas volume is shown, for simplicity). With the exception of the dipole moment (Figure 3D), all other properties can be correlated with the experimental k_H values, yielding a simple bell-shaped dependence, which includes not only saturated aliphatic carbonyl derivatives but also most of the other categories, except hydroxycarbonyls. Data for hydroxycarbonyl–PFBHA derivatives exhibit k_H values that are significantly lower than those of other derivatives with similar molecular volume, surface area, or polarizability. This can be explained by the presence of a hydroxyl group in these molecules, which provides additional stability in water due to hydrogen bonding, thus reducing their tendency to escape from solution (i.e., fugacity). The only important difference between the correlation based on polarizability and those corresponding to the solute volume and surface area is related with the values for the 9-fluorenone derivative (represented with a white triangle in Figure 3). This is a more polarizable compound as compared with the rest of the solutes due to its larger number of π electrons, and it behaves as an outlier in the polarizability plot.

Table 5. Temperature Effect on the Henry's Law Constant (k_H) and the Air−Water Partition Coefficient (k_{aw}) for Eight Carbonyl−PFBHA Derivatives in the Range (5 to 25) °C

	k_H/Pa·m^3·mol^{-1}			10^3k_{aw}			ΔH^∞	ΔS^∞
	T = 298 K	T = 288 K	T = 278 K	T = 298 K	T = 288 K	T = 278 K	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
acetone	90.3 ± 5.9	48.5 ± 3.1	33.4 ± 3.6	36.9	20.5	14.6	31.7	78.6
acrolein	105.2 ± 4.2	48.5 ± 7.2	26.7 ± 7.4	43.0	20.5	11.7	44.6	123.5
2-butanone	215 ± 12	90.0 ± 6.7	46.7 ± 8.8	88.1	38.1	20.4	50.0	147.3
crotonaldehyde	147 ± 15	100.4 ± 4.5	60.1 ± 6.0	60.3	42.5	26.3	28.5	72.4
formaldehyde	61.3 ± 6.2	27.7 ± 6.1	10.0 ± 3.8	25.0	11.7	4.3	59.9	170.9
acetaldehyde	52.9 ± 4.9	20.8 ± 5.2	13.4 ± 3.9	21.6	8.81	5.8	44.7	117.6
2-pentanone	268 ± 41	183 ± 29	147 ± 23	109.7	77.7	64.4	18.2	42.6
benzaldehyde	199 ± 21	162 ± 29	113 ± 27	81.6	68.5	49.8	17.0	36.5

A simple mathematical description of the dependence of k_H with V_m, S_m, and α can be obtained by Gaussian fitting of the data sets plotted in Figure 3A−C with the equation

$$k_H = a + b\exp\left[-0.5\left(\frac{(X-c)}{d}\right)^2\right] \tag{8}$$

where X indicates V_m, S_m, or α. The fitting parameters a, b, c, and d corresponding to eq 8 as applied to the data in Figure 3A−C are presented in Table 4. Considering the effect of the activity coefficient (γ^∞) and the vapor pressure (p_g°) on k_H discussed above (see eq 7), the initial growth observed for low molecular weight derivatives can be attributed to a regime in which the increase in γ^∞ predominates, while the declining k_H values for higher molecular weights arise from the exponential decay of the vapor pressure (p_g°). The Gaussian curves exhibit good correlation with most saturated aliphatic−, unsaturated aliphatic−, and aromatic carbonyl−PFBHA derivatives, as well as those of dicarbonyls. The polarizability (α) seems to present a slightly better performance as a molecular descriptor ($R^2 = 0.870$) as compared with the molecular volume (V_m, $R^2 = 0.859$) and surface area (S_m, $R^2 = 0.787$). Data for hydroxycarbonyl−PFBHA derivatives were not used in the correlation with any molecular descriptor, while the polyaromatic derivative was excluded only in the case of α, where it behaved as an outlier.

The three descriptors V_m, S_m, and α have a high correlation among each other. It is, therefore, not surprising to see that k_H versus each of the three descriptors exhibits a similar bell-shaped relationship. The dipole moment instead proved to be an extremely insensitive descriptor, as can be seen in Figure 3D. Its value is essentially dominated by the PFBHA common core of the structure, with negative partial charges located on the N atom (about −0.2 e) and on the five F atoms (−0.06 to −0.08 e). The glyoxal derivative contains two PFBHA units, exhibiting the lowest molecular dipole moment for symmetry reasons. Hydroxycarbonyl derivatives also present a lower molecular dipole, due to the partial negative charges located on the O atoms (about −0.3 e).

***Temperature Dependence from 5 to 25* °C.** The effect of temperature on k_H was evaluated for the PFBHA derivatives of acetone, acrolein, 2-butanone, crotonaldehyde, formaldehyde, acetaldehyde, 2-pentanone, and benzaldehyde. From the slope and intercept of the linear regression of ln k_{aw} versus T^{-1}, we estimate values of ΔH^∞ and ΔS^∞, according to eq 4. These parameters, together with the corresponding k_H and k_{aw}, are reported in Table 5. Small variations were observed in the temperature dependence parameters (in the ranges $17 < \Delta H^\infty/\text{kJ·mol}^{-1} < 60$ and $36 < \Delta S^\infty/\text{J·K}^{-1}\text{·mol}^{-1} < 170$, respectively). The more volatile derivatives among the analyzed solutes (those corresponding to 2-pentanone and benzaldehyde) were less sensitive to temperature changes (i.e., lower ΔH^∞). The estimated ΔH^∞ and ΔS^∞ are of the same order of magnitude as that of values reported for the temperature dependence of Henry's law constants for PCBs.[39]

Performance of Water-Based Air Samplers with in Situ PFBHA Derivatization. The values reported in the literature for k_H of most of the underivatized (i.e., free) carbonyls studied in the present work are reported in Table 1 (data for 3-hydroxy-3-methyl-2-butanone were not available). In almost all cases, with the single exception of decanal, the reported Henry's law constants of the free carbonyls were lower than those determined for their PFBHA derivatives in the present work. In some extreme cases, corresponding to low molecular weight solutes and hydroxylated carbonyls, the k_H values of the free carbonyls are 3 to 5 orders of magnitude lower than those of derivatized carbonyls. This indicates that PFBHA derivatives can be considerably more volatile than the free analyte, and therefore the risk of volatilization losses during sampling is higher when PFBHA is added to the collection solution. This fact underscores the importance of evaluating the volatilization rates, on the basis of the Henry's constant values of both free and derivatized carbonyls. In previous research, we report collection efficiencies of 0.94 for glycolaldehyde, 0.86 for hydroxyacetone and glyoxal, and 0.83 for methylglyoxal when sampling for 10 min using two mist chambers in series. The Henry's law constants for the free carbonyls (or "effective" k_H values, which include hydration products) were lower than 0.03 Pa·m^3·mol^{-1} (or higher than 3000 M·atm^{-1}). We also reported breakthrough of acrolein, methacrolein, crotoaldehyde, p-tolualdehyde, methyl glyoxal, benzaldehyde, hydroxy acetone, and glycolaldehyde among other analytes when sampling for 4 h when using four impingers in series.[1,19] The high collection efficiencies when using the mist chambers indicate that, at least for the considered analytes, the higher volatility of their PFBHA derivatives does not seem to affect dramatically the observed collection efficiency. Furthermore, the empirical collection efficiency in mist chambers correlated well with a theoretical model that did not take into account the derivatization of the analytes.[1] Considering that the sampling time with the mist chamber is very short (10 min), these results suggest that the PFBHA derivatization of carbonyls is a slow reaction and that volatilization of a carbonyl−PFBHA derivative does not affect the collection efficiency. In contrast, when using impingers which utilize longer sampling times (e.g., 4−8 h), the presence of the analytes in the fourth impinger in the previous work[19] suggests that formation of the PFBHA derivatives and subsequent volatilization can become a problem when long sampling times are involved. Clearly, obtaining quantitative information about the kinetics of PFBHA derivatization is an important step toward understanding processes affecting the collection efficiency for methods that rely on in situ PFBHA derivatization of airborne carbonyls.

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