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Apparent Partition Coefficients of 15 Carbonyl Compounds between Air and Seawater and between Air and Freshwater; Implications for Air-Sea Exchange

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■ Apparent partition coefficients (K^* , in M/atm) of 15 carbonyl compounds between water and air were determined as a function of temperature, salinity, and pH, using a bubble column technique. Values for K^* decrease with increasing carbon number of alkanals; e.g., at 25 °C apparent partition coefficients between air and seawater range from 3710 for formaldehyde and 13.1 for acetaldehyde to 0.181 for decanal. Where overlap exists, our data are in good agreement with literature values. $\log K^*$ was found to be highly temperature dependent, varying linearly with $1/T$ for all compounds studied. The salinity effect on K^* increases with increasing molecular weight; $K^*(\text{seawater})/K^*(\text{freshwater})$ ratios range from close to 1 for formaldehyde and acetaldehyde to less than 0.3 for nonanal and decanal. The effect of pH in the range of 4-8 on K^* was found to be negligible. This study presents the most complete data set of carbonyl partition coefficients to date and should facilitate modeling of exchange of these compounds between gas and aqueous phases. Some implications of our results for air-sea exchange of carbonyl compounds are discussed.

Introduction

Carbonyl compounds occur in the atmosphere as a result of photooxidation of anthropogenic and natural organic compounds (1), and also incomplete combustion of fossil fuel (1). These compounds are active participants in atmospheric chemical reactions in both gas and liquid phases, where they play key roles in cloud chemistry and in the speciation of sulfur and nitrogen compounds (1-3). Carbonyl compounds are also receiving wide attention as pollutants both in the atmosphere (1, 4) and in treated or contaminated waters (4). In natural waters, these compounds are produced as photodegradation products of humic substances and unsaturated fatty acids (5-8) and during fermentation in anoxic environments (9). Photolysis in the atmosphere (1) and biological uptake in natural waters (10) are major sinks for carbonyl compounds. It has been shown that photodegradation of marine dissolved organic matter (DOM) into low molecular weight (LMW) compounds (e.g., carbonyl compounds and keto acids) coupled with biological consumption of these LMW products is a major path for refractory DOM removal in the ocean (11).

The exchange of carbonyl compounds between air and natural waters links processes in both systems (12, 13). The direction and magnitude of flux of a compound across the air-water interface, except for wet precipitation, are dependent on the concentration gradient between the two phases, $(K^*P - C_{aq})$, where P is partial pressure and C_{aq} is the concentration of the compound in water, and K^* (in M/atm) is the apparent partition coefficient.

Past studies of the exchange of carbonyl compounds between air and seawater have been hindered because of the scarcity of published partition coefficients for these compounds. A few of these coefficients have been determined between air and freshwater (14-16), but none between air and seawater. In this paper, we describe a convenient method for measuring carbonyl partition coefficients between air and aqueous solutions, including natural seawater. We measured partition coefficients for 15 carbonyl compounds as a function of temperature, salinity, and pH. Using this data set, together with measured concentrations of carbonyl compounds in surface seawater and marine air, we predict the direction of their net air-sea exchange.

Experimental Section

Materials. Acetonitrile used was HPLC grade (Burdick and Jackson, Muskegon, MI); water was obtained from a Millipore Q water system with an Organex attachment (Millipore, Milford, MA). 2,4-Dinitrophenylhydrazine (DNPH) reagent was from Sigma (St. Louis, MO) and was recrystallized twice from acetonitrile. Carbon tetrachloride used for DNPH solution purification was Burdick and Jackson high-purity grade. Carbonyl compounds were obtained from Aldrich (Milwaukee, WI) or Sigma. Stock solutions of 10-200 mM were made in acetonitrile or 50:50 acetonitrile-water solution.

Seawater (salinity $35 \pm 1\text{‰}$) was collected from Biscayne Bay, and was filtered through a 0.22- μm nylon membrane filter (MSI, Magna, Honeoye Falls, NY).

Carbonyl Equilibration System. The system used for establishing carbonyl equilibrium between air and aqueous solution is shown in Figure 1. In contrast to most previously reported systems, our system is simple and inexpensive to build, and all parts are commercially available. Two 1.2-L glass reagent bottles (Wheaton, 16-cm height) were filled with aqueous test solutions of carbonyl compounds. Concentrations of carbonyl compounds spiked into test solutions ranged from 0.05 to 5 μM for C2-C10 alkanals, ketones, and benzaldehyde and 10 to 100 μM for formaldehyde, glyoxal, and methylglyoxal. The headspace of each bottle was 5-10 mL. The bottles were equipped with polypropylene caps (Dionex, Sunnyvale, CA), which were made air-tight with Tefzel O-rings. The two bottles were connected in series by a short piece of Teflon tubing (~ 15 cm long). Stainless steel frits were used to produce fine bubbles (<0.1 -mm diameter) in the bottles. Three DNPH-coated Sep-Pak C18 cartridges (Waters, Milford, MA) were connected in series to the inlet of the system to strip carbonyl compounds from the incoming air (17). The outlet of the second bottle was connected to a 0.2- μm hydrophobic Teflon filter (Millex-FG, Millipore, Milford, MA) to remove water droplets and then to a DNPH-coated Sep-Pak cartridge to collect carbonyl compounds in the equilibrated air. Laboratory air was pumped through this system by a diaphragm pump (Model TD-4X2S, Brailsford & Co., Rye, NY) at a flow rate of <150 mL/min. In order to minimize wall effects, the system was conditioned by

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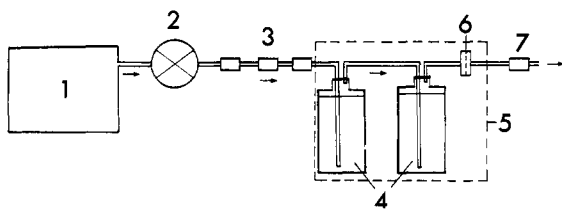


Figure 1. Apparatus for equilibration of carbonyl compounds between air and aqueous solution. (1) Collapsible polyethylene container, (2) air pump, (3) carbonyl stripper cartridges, (4) aqueous test solution, (5) water bath, (6) Teflon filter, (7) carbonyl collecting cartridge.

pumping equilibrated air for 10–15 min before samples were collected. The two bottles and the Teflon filter were immersed in a water bath at the desired temperature ($\pm 0.1^\circ\text{C}$).

Collapsible polyethylene containers, 1, 4, and 10 L, were used to measure the volume of air pumped through the system. They were filled with air against atmospheric pressure and then connected to the inlet of air pump. In this way, we were able to reproducibly pump an exact volume of air through the system for each run. The volume pumped through the system was 1–2 L for C5–C10 alkanals, 4 L for C2–C6 alkanals, ketones, and benzaldehyde, and 10–20 L for formaldehyde, glyoxal, and methylglyoxal.

Carbonyl Analyses. Carbonyl concentrations in aqueous solutions used for partition studies were determined by direct injection of samples into the HPLC system after derivatization with DNPH (8, 18). Briefly, a 5-mL aqueous sample was pipetted into a 7-mL Teflon vial followed by 100 μL of purified DNPH solution (20 mg of DNPH/15 mL of 20% acetonitrile in acidic aqueous solution, extracted twice with CCl_4). Aqueous samples were injected into the HPLC system with a 2-mL sample loop 1 h after derivatization.

Sampling and analysis of carbonyl compounds in air samples are described elsewhere (17). Briefly, carbonyl compounds were collected on a DNPH-coated Sep-Pak C18 cartridge by pumping ($<150\text{ mL/min}$) the equilibrated air through it. The carbonyl-DNPH derivatives and unreacted reagent were eluted off the cartridge with 2 mL of acetonitrile. The eluate was collected in a 5-mL Teflon vial and 50 μL was injected directly into the HPLC system within 1 h after elution. The recovery of gas-phase carbonyl compounds was $>98\%$, even for the most volatile species (17).

The HPLC system consisted of an E-Lab Model 2020 gradient programmer and data acquisition system (OMS Tech, Miami, FL) installed in an IBM-compatible PC, an Eldex Model AA pump (Eldex Laboratories, Menlo Park, CA), a six-port Valco injector (Valco Instruments, Houston, TX) with either a 50- μL or 2-mL sample loop, and a Radial compression separation system with an 8-mm-i.d. C18 reversed-phase Radial-Pak cartridge (type 8 NVC 184, Waters). An Isco Model V4 variable-wavelength absorbance detector (Isco, Lincoln, NE) was used to detect carbonyl-DNPH derivatives at 370 nm. The mobile-phase gradient was generated by a solenoid valve controlled by the E-Lab gradient programmer. A two-solvent gradient elution was used: 10% acetonitrile aqueous solution (A) and acetonitrile (B). The gradient program was as follows: isocratic at 36% B for 2 min, 36% B to 53% B in 4 min, isocratic at 45% B for 8 min, 45% B to 80% B in 10 min, and then isocratic at 100% B for 15 min. The flow rate was 1.5 mL/min and separations were performed at ambient temperature, $\sim 22^\circ\text{C}$.

Field Data Collection. Carbonyl compounds in marine air were measured during three oceanographic cruises to the Caribbean Sea and Sargasso Sea between October 1988

and March 1989 on board the R/V Columbus Iselin. Details of the sampling procedure have been described elsewhere (17, 19). In brief, atmospheric carbonyl compounds were trapped onto two DNPH-coated Sep-Pak C18 cartridges connected in series. Air samples were drawn through the cartridges at a flow rate of 0.5–0.7 L/min. The trapping efficiency was $>95\%$ for all compounds studied and the overall procedural blank was $<0.07\text{ ppb}$ for formaldehyde and $<0.02\text{ ppb}$ for other compounds for an air sample of 100 L (17). Samples were collected at a height of 10 m above the sea surface during steaming or, while on station, upwind of any contamination source, e.g., the ship's exhaust.

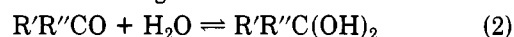
Carbonyl compounds in seawater were measured during two cruises to the Sargasso Sea in March and November 1989 on board the R/V Columbus Iselin. The sampling technique is described in detail elsewhere (8, 18). For formaldehyde, acetaldehyde, and glyoxal, seawater samples were directly injected into the HPLC system after DNPH derivatization (8, 18). For other compounds the concentrations were often too low to be measured by direct injection, therefore preconcentration was necessary (18). Derivatized seawater (20 mL) was drawn through a pre-cleaned Sep-Pak C18 cartridge. The cartridge was rinsed with 15 mL of 17% acetonitrile aqueous solution (pH 2.5) to eliminate the excess reagent and then eluted with 1 mL of acetonitrile to remove the trapped carbonyl hydrazones. Calibration was made by standard addition. Surface seawater samples were collected either with Teflon-coated Go-Flo bottles (General Oceanics, Ft. Lauderdale, FL) or from a Teflon-lined pumping system from 2-m depth.

Results and Discussion

The partition coefficient of a carbonyl compound, $R/R''\text{CO}$, is defined as the ratio of the concentration of this compound in aqueous phase to its partial pressure in gas phase at equilibrium:

$$K = [R/R''\text{CO}]_{\text{aq}}/P \quad (\text{M/atm}) \quad (1)$$

where $[R/R''\text{CO}]$ is the concentration of the free molecule in aqueous solution and P is its partial pressure in gas phase. Carbonyl compounds, especially low molecular weight simple aldehydes and dicarbonyl compounds, are hydrated to different degrees in water:



e.g., $>99\%$ of formaldehyde (20) and $\sim 50\%$ of acetaldehyde (21) are in diol forms. Therefore, it is often practical to use apparent partition coefficients:

$$K^* = \frac{[R/R''\text{CO}]_{\text{aq}} + [R/R''\text{C}(\text{OH})_2]_{\text{aq}}}{P} \quad (\text{M/atm}) \quad (3)$$

The analytical technique employed in this study measures total carbonyl concentrations in aqueous solution. Thus, the data presented here are apparent partition coefficients.

Reproducibility and Wall Effects. Five air samples were collected sequentially after passing through the equilibration system containing an aqueous solution of C2–C7 alkanals, acetone, butanone, and benzaldehyde. The concentrations of these compounds in the five air samples differed by less than 7% relative standard deviation (RSD), which is only slightly higher than the 5% RSD of the HPLC method. These results indicated that the experimental system was set up correctly and that it was able to generate reproducible results. In addition, there were no systematic differences in carbonyl concentrations between the first and last samples, suggesting that wall effects, i.e., adsorption/reaction of carbonyl compounds with the walls of the containers, connecting tubing,

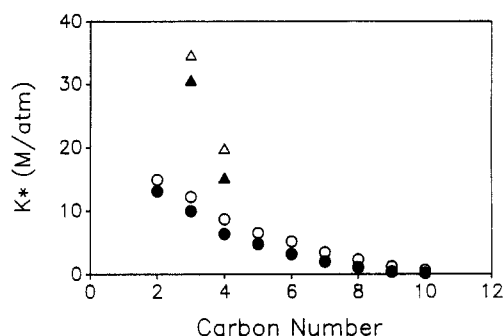


Figure 2. Plot of partition coefficients of alkanals (circles) and ketones (triangles) between air and freshwater (open symbols) and between air and seawater (closed symbols).

and the outlet filter, were unimportant after the system was conditioned.

Equilibration Test. To determine whether air leaving the bottles was in equilibrium with the aqueous solution, two tests were performed. First, carbonyl concentrations in air were measured after passage through one, two, or three bottles of aqueous solution with a constant flow rate of 150 mL/min. The differences in carbonyl concentrations among the three sets of samples were within analytical error, less than 7% RSD for all the compounds. In the second test, a constant volume of air was pumped through two bottles at flow rates of 100, 200, 300, and 400 mL/min. Again, concentrations of all carbonyl compounds in the air samples were within the analytical error, i.e., less than 7% RSD, over the flow rate range tested. Therefore, we conclude that air bubbled through two bottles of solution is in equilibrium with the aqueous phase. These results are in agreement with past studies that used similar bubble column techniques (16, 22).

Data Compilation. Table I lists apparent partition coefficients of 15 carbonyl compounds between air and freshwater and between air and seawater at different salinities and temperatures. These values represent averages of four to nine measurements, except for glyoxal and methylglyoxal where only two runs were made. Figure 2 shows apparent partition coefficients of alkanals from C1 to C10, acetone, and butanone in freshwater and seawater. Decreasing K^* values with increasing molecular weight reflect the lower solubility of higher carbonyl compounds in the aqueous phase relative to low molecular weight carbonyl compounds under the same partial pressure. This trend is in agreement with results of Buttery et al. (14). Solubilities of acetone and butanone are higher than those of their corresponding alkanals because of differences in polarities; i.e., ketones form stronger hydrogen bonds with water (23).

Figure 3 is a plot of the freshwater data from the present study vs those available in the literature (14–16, 20). The straight line represents a one-to-one match of all data. Despite the widely different methods used by different authors, the agreement is remarkable, generally deviating less than 20% for most carbonyl compounds, and ~30% for acetone. This excellent agreement confirms the reliability of our comparatively simple method. It further indicates that our data can be used to accurately evaluate the effects of temperature, salinity, and pH, for which there are few or no literature values.

Effects of pH. Compounds used to examine the effect of pH on apparent partition coefficients were formaldehyde, acetaldehyde, hexanal, nonanal, acetone, and benzaldehyde. As expected, no significant differences in apparent partition coefficients between pH 4 and 8 were found for these nonionic compounds. This result is in

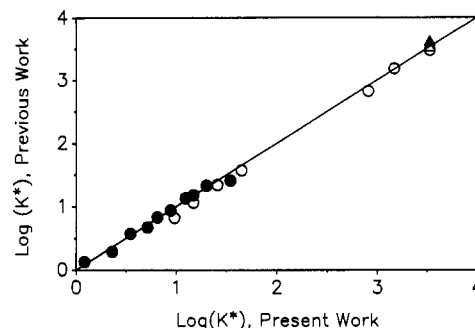


Figure 3. Agreement between the air-freshwater carbonyl partition coefficient data set of the present study and those of previous studies. The solid line represents a one-to-one correspondence for all the data. Symbols: (○) formaldehyde at 25, 35, and 45 °C, benzaldehyde at 25 and 35 °C, acetaldehyde at 25 and 35 °C (16); (●) acetone, butanone, and C2–C9 alkanals at 25 °C (14); (Δ) formaldehyde at 25 °C (20); (▲) formaldehyde at 25 °C (15).

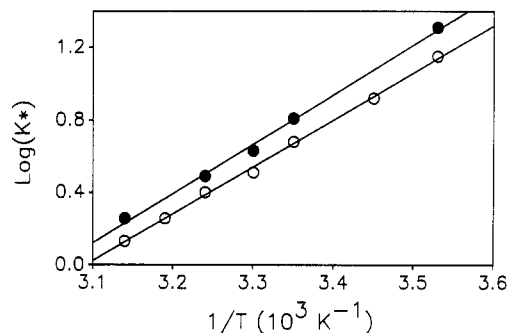


Figure 4. $\log K^* - 1/T$ relationship for valeraldehyde. (○) seawater, (●) freshwater.

agreement with previous results for formaldehyde (15, 16) and for acetone and butanone (24). Since the pH of seawater is within a narrow range of 7.5–8.3, there is no significant pH effect for carbonyl compounds of interest in seawater.

Effect of Temperature. The relation between the apparent partition coefficient of a carbonyl compound (eq 3) and temperature can be expressed by eq 4, where K_1

$$K^* = K_1 \exp(K_2/T) \quad (\text{M/atm}) \quad (4)$$

and K_2 are constants that take into account the partition equilibrium, as well as hydration and other possible equilibria. Equation 4 can be rewritten as

$$\log K^* = A + B/T \quad (5)$$

where A and B are constants. A linear relationship is obtained by plotting $\log K^*$ vs $1/T$.

Table II summarizes the best fit parameters of our data to eq 5; and Figure 4 is the plot of $\log K^*$ for pentanal vs $1/T$ as an example. All our data fit eq 5 with $R^2 > 0.99$. These relationships are useful for estimating apparent partition coefficients at different temperatures.

Effect of Salinity. The effect of salt on the solubility of gases in seawater has been studied theoretically for a variety of small gas molecules, e.g., He, Ne, Ar, O₂, and N₂ (25). According to scaled-particle theory (25), the presence of salt in aqueous solution has two important effects on gas solubility: (1) a "salting-out" effect as a result of change in water structure in the vicinity of the solute and (2) shifting the equilibria of solute-water interactions, e.g., hydration and dissociation, which tends to increase gas solubility. The salting-out effect is generally more important for larger, hydrophobic molecules, while the effect of chemical equilibrium shifting is more important for reactive species (25).

Table I. Apparent Partition Coefficients (M/atm)^a of Carbonyl Compounds between Air and Aqueous Solutions Containing Different Percentages of Seawater

temp, °C	seawater composition, %					temp, °C	seawater composition, %				
	0	25	50	75	100		0	25	50	75	100
Formaldehyde ($\times 10^{-3}$)						Heptanal					
10	9.9 ± 1.1		10.5 ± 0.8		13.7 ± 1.0	10	12.4 ± 0.5		8.9 ± 0.7		6.8 ± 0.6
17					7.9 ± 0.4	17					4.1 ± 0.1
25	3.4 ± 0.3	3.8 ± 0.2	3.4 ± 0.1	3.6 ± 0.1	3.7 ± 0.4	25	3.4 ± 0.2		2.3 ± 0.1		2.0 ± 0.1
30	2.0 ± 0.1				2.5 ± 0.2	35	1.4 ± 0.1		1.2 ± 0.1		1.0 ± 0.1
35	1.5 ± 0.1		1.7 ± 0.1		1.9 ± 0.1	45	0.70 ± 0.02				0.51 ± 0.03
40	1.1 ± 0.0										
45	0.81 ± 0.04	0.88 ± 0.02	0.88 ± 0.01	0.87 ± 0.01	0.88 ± 0.06	Octanal					
						10	7.8 ± 0.7		4.6 ± 0.4		3.1 ± 0.3
Acetaldehyde						17					2.0 ± 0.2
10	44.5 ± 1.5		41.1 ± 3.2		32.2 ± 2.2	25	2.3 ± 0.2		1.3 ± 0.1		1.1 ± 0.1
17					19.6 ± 1.1	35	0.92 ± 0.02		0.79 ± 0.04		0.59 ± 0.05
25	14.9 ± 1.1	14.4 ± 1.2	14.1 ± 1.3	13.6 ± 1.3	13.1 ± 1.0	45	0.45 ± 0.01				0.28 ± 0.02
30	12.3 ± 0.8				10.9 ± 0.7						
35	9.6 ± 0.8		9.5 ± 0.8		8.6 ± 0.6	Nonanal					
40					6.8 ± 0.4	10	3.1 ± 0.3		1.6 ± 0.2		0.98 ± 0.08
45	6.5 ± 0.1	6.2 ± 0.1	5.9 ± 0.1	5.9 ± 0.2	5.7 ± 0.1	17					0.63 ± 0.07
Propanal						25	1.2 ± 0.1		0.51 ± 0.03		0.38 ± 0.03
10	38.9 ± 0.2		34.9 ± 1.9		29.9 ± 1.5	35	0.46 ± 0.03				0.18 ± 0.01
17					15.6 ± 1.7	45	0.24 ± 0.01				0.10 ± 0.005
25	12.2 ± 0.8	12.3 ± 1.0	11.9 ± 0.5	11.5 ± 0.5	10.0 ± 0.6	Decanal					
30	9.5 ± 0.5				8.0 ± 0.1	25	0.63 ± 0.05		0.23 ± 0.02		0.18 ± 0.021
35	7.2 ± 0.5		6.9 ± 0.1		6.2 ± 0.1	35	0.22 ± 0.02				0.074 ± 0.002
40					4.6 ± 0.2	45	0.10 ± 0.01				0.030 ± 0.003
45	4.3 ± 0.3				3.6 ± 0.2	Benzaldehyde					
Butanal						10	92.5 ± 1.1		85.8 ± 0.8		75.7 ± 0.2
10	31.3 ± 2.2		29.8 ± 1.0		23.5 ± 1.5	17					51.0 ± 0.9
17					11.7 ± 0.8	25	44.4 ± 3.7	39.9 ± 1.1	39.2 ± 2.1	37.7 ± 4.1	33.5 ± 2.9
25	8.7 ± 0.4	8.2 ± 0.3	7.5 ± 0.4	7.25 ± 0.53	6.3 ± 0.4	30	33.6 ± 3.0				24.2 ± 1.8
30	6.4 ± 0.2				4.9 ± 0.3	35	25.7 ± 1.5		20.4 ± 0.5		17.5 ± 0.9
35	4.9 ± 0.3		4.6 ± 0.3		3.6 ± 0.1	40					13.8 ± 1.2
40					2.6 ± 0.1	45	15.8 ± 0.8		12.3 ± 0.8	11.8 ± 1.1	10.9 ± 0.8
45	2.8 ± 0.1		2.7 ± 0.2		2.0 ± 0.1	Acetone					
Pentanal						10	71.3 ± 3.1		65.6 ± 4.4		58.4 ± 5.1
10	20.5 ± 1.3		17.3 ± 0.8		14.2 ± 1.0	17					43.0 ± 3.4
17					8.3 ± 0.2	25	34.6 ± 0.6	32.3 ± 1.8	31.8 ± 2.4	31.5 ± 1.5	30.6 ± 2.9
25	6.5 ± 0.3	5.9 ± 0.2	5.7 ± 0.4	5.2 ± 0.2	4.7 ± 0.3	30	27.7 ± 2.5				25.1 ± 1.5
30	4.2 ± 0.1				3.2 ± 0.2	35	22.1 ± 1.8		21.8 ± 1.6		21.0 ± 0.8
35	3.1 ± 0.2		3.0 ± 0.2		2.5 ± 0.2	40					18.9 ± 0.6
40					1.8 ± 0.1	45	16.4 ± 1.1		16.3 ± 1.7	15.6 ± 1.4	14.80 ± 0.9
45	1.8 ± 0.1	1.8 ± 0.1	1.7 ± 0.1	1.6 ± 0.1	1.4 ± 0.1	Butanone					
Hexanal						10	49.0 ± 0.8		41.8 ± 2.1		37.5 ± 2.4
10	15.9 ± 1.2		13.1 ± 0.4		9.8 ± 0.1	17					25.7 ± 2.0
17					6.3 ± 0.5	25	19.8 ± 1.4	18.1 ± 1.3	16.9 ± 0.5	16.4 ± 0.8	15.2 ± 1.3
25	5.2 ± 0.5	4.4 ± 0.4	3.4 ± 0.3	3.6 ± 0.2	3.2 ± 0.1	30	14.1 ± 0.2				11.6 ± 0.3
30	3.2 ± 0.3				2.3 ± 0.1	35	10.9 ± 0.5		10.1 ± 1.0		9.4 ± 0.9
35	2.3 ± 0.2		2.1 ± 0.2		1.7 ± 0.1	40					7.2 ± 0.3
40					1.3 ± 0.1	45	7.1 ± 0.7		6.2 ± 0.3		5.6 ± 0.2
45	1.3 ± 0.1	1.3 ± 0.1	1.3 ± 0.1	1.0 ± 0.0	0.91 ± 0.05	Glyoxal ($\times 10^{-5}$)					
						25					3.6 ± 2.1
						Methylglyoxal ($\times 10^{-4}$)					
						25					3.2 ± 1.3

^a Mean $\pm 1\sigma$, $n > 4$, except $n = 2$ for glyoxal and methylglyoxal.

Table II. Best Fit Parameters for Equation 5: $\log K^* = A + B/T$ for Estimating the Temperature Dependence (in K) of the Apparent Partition Coefficient, K^* , of Carbonyl Compounds between Air and Water

compound	aqueous phase	A	B	r ²	compound	aqueous phase	A	B	r ²
formaldehyde	seawater	-6.7	3069	0.997	octanal	seawater	-8.84	2645	0.997
formaldehyde	freshwater	-6.0	2844	0.995	octanal	freshwater	-10.4	3214	0.998
acetaldehyde	seawater	-5.21	1894	0.994	nonanal	seawater	-9.01	2555	0.997
acetaldehyde	freshwater	-6.03	2164	0.989	nonanal	freshwater	-9.81	2929	0.998
propanal	seawater	-6.60	2273	0.992	decanal	seawater	-13.1	3690	0.999
propanal	freshwater	-7.15	2467	0.994	decanal	freshwater	-12.8	3740	0.994
butanal	seawater	-8.20	2698	0.993	benzaldehyde	seawater	-5.90	2207	0.998
butanal	freshwater	-8.07	2701	0.992	benzaldehyde	freshwater	-5.00	1977	0.998
pentanal	seawater	-8.15	2633	0.999	acetone	seawater	-3.60	1518	0.999
pentanal	freshwater	-8.42	2753	0.997	acetone	freshwater	-5.00	1977	0.998
hexanal	seawater	-8.35	2645	0.997	butanone	seawater	-5.97	2138	0.998
hexanal	freshwater	-8.76	2819	0.995	butanone	freshwater	-6.03	2184	0.996
heptanal	seawater	-9.45	2913	0.998					
heptanal	freshwater	-10.4	3252	0.998					

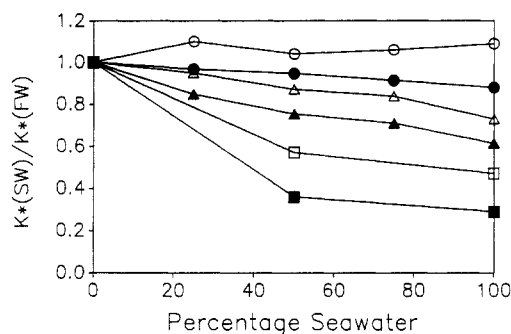


Figure 5. Effect of sea salt on apparent partition coefficients of carbonyl compounds at 25 °C. (O) formaldehyde, (●) acetaldehyde, (Δ) butyraldehyde, (▲) hexanal, (□) octanal, (■) decanal.

Figure 5 shows the ratio of apparent partition coefficients of alkanals in seawater to those in freshwater, as a function of percentage of seawater in the mixtures. The results are in general agreement with theory. The ratio is close to 1 for lower aldehydes like formaldehyde and acetaldehyde, suggesting that the salting-out effect at the ionic strengths examined is not important for these compounds or that there is balance between the two opposite effects, salting-out and hydration equilibrium shifting. This result is also in agreement with that of Dong and Dasgupta (15), who found that ionic strength has little effect on gaseous formaldehyde solubility in water. The salting-out effect becomes pronounced for larger molecules. For decanal, the apparent partition coefficient between air and seawater is only ~30% of that between air and freshwater. Therefore, the use of partition coefficients between air and freshwater in air-sea exchange studies of higher aldehydes would result in significant errors.

Air-Sea Equilibria/Disequilibria of Carbonyl Compounds. We used our partition coefficients, together with measured carbonyl concentrations, to determine whether the ocean and atmosphere are in equilibrium with respect to these compounds and to predict the direction of net exchange across the air-sea interface. Concentrations of carbonyl compounds, except for formaldehyde (12, 26, 27) and acetone (28) have not been previously reported for marine air due to technical difficulties. With our sampling technique, we were able to measure ambient carbonyl concentrations in marine air (17, 19). Concentrations over the Caribbean Sea and Sargasso Sea were between 0.2 and 2.5 ppb for LMW carbonyl compounds (formaldehyde, acetaldehyde, and acetone), and between tens and hundreds parts-per-trillion for other compounds (19). Formaldehyde and acetone concentrations compared well to values reported in the literature, e.g., 0.1–0.6 ppb for formaldehyde and 0.4 ppb for acetone, in clean air over the open ocean (12, 26–28) to low ppb levels in coastal regions under land influence (27). For consideration of air-sea equilibria/disequilibria of carbonyl compounds, only typical concentrations of these compounds in clean air over open regions are used in Table III (19).

In seawater, formaldehyde, acetaldehyde, and acetone were present at ~10 nM, while others were at low or subnanomolar levels (Table III). These values are in good agreement with previously reported concentrations of LMW carbonyl compounds (8, 18). Predicted carbonyl concentrations in seawater, when in equilibrium with the atmosphere, were calculated by using measured atmospheric concentrations of these compounds and their partition coefficients obtained in this study (Table III). From these calculations it is apparent that for compounds with high solubility (e.g., formaldehyde, glyoxal, and methylglyoxal) and with low solubility (e.g., C8–C10 aldehydes),

Table III. Typical Carbonyl Concentrations in Clean Marine Air, and Predicted and Measured Concentrations in Surface Open Ocean Seawater

compounds	concn in air, ^a ppb	predicted concn in seawater, ^b nM	measured concn in seawater, ^c nM
formaldehyde	0.4	1500	2–40
acetaldehyde	0.3	4	2–15
propanal	0.1	1	0.4–3
butanal	0.08	0.5	0.3–2
pentanal	0.1	0.5	0.2–5
hexanal	0.1	0.3	0.2–0.6
heptanal	0.1	0.2	0.2–0.5
octanal	0.1	0.1	0.2–0.7
nonanal	0.15	0.06	0.2–1
decanal	0.1	0.02	0.2–0.8
benzaldehyde	~0.01	0.3	ND ^c
acetone	0.3	10	3–50
butanone	0.05	0.8	0.5–2
glyoxal	0.08	30000	0.5–5
methylglyoxal	~0.01	300	0.1–1.5

^a Typical carbonyl concentrations in the air over open Caribbean Sea and Sargasso Sea. ^b Predicted concentrations in seawater in equilibrium with atmosphere: $[R'R''CO] = K^*P$ at 25 °C. ^c Carbonyl concentrations measured in South Sargasso Sea surface water. ND, not determined.

surface seawater is completely out of equilibrium with the atmosphere. The direction of net flux is always from the atmosphere to the ocean for the former group of compounds and the reverse for the latter group. For the other compounds (Table III), the direction of flux will depend on a number of environmental factors, e.g., the area of study, time of day and season, cloud cover, wind direction, source of air mass, and temperature.

Acknowledgments

We thank J. M. C. Plane and E. S. Saltzman for valuable discussions during the course of this study.

Registry No. Seawater, 7732-18-5; formaldehyde, 50-00-0; acetaldehyde, 75-07-0; propanal, 123-38-6; butanal, 123-72-8; pentanal, 110-62-3; hexanal, 66-25-1; heptanal, 111-71-7; octanal, 124-13-0; nonanal, 124-19-6; decanal, 112-31-2; benzaldehyde, 100-52-7; acetone, 67-64-1; butanone, 78-93-3; glyoxal, 107-22-2; methylglyoxal, 78-98-8.

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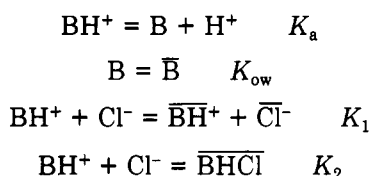
Received for review August 8, 1989. Revised manuscript received March 6, 1990. Accepted July 24, 1990. This work was supported by grants from the Chemical Oceanography Program of the U.S. National Science Foundation (OCE 86-13940 and OCE 89-17709).

Effect of pH and KCl Concentration on the Octanol-Water Distribution of Methylanilines

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■ The distributions of aniline, 4-methylaniline, 3,4-dimethylaniline, and 2,4,5-trimethylaniline between octanol and water were determined as a function of pH and KCl concentration in the aqueous phase. The data were interpreted in terms of a multicomponent equilibrium model with anilinium in the water-saturated octanol as free ions and ion pairs. The reactions are



where B represents the organic base, and the overbar denotes a species in the octanol phase. The implications of these results to the use of the octanol-water reference system for organic bases and to the sorbent-water distribution of organic bases in the environment is discussed.

Introduction

Several hydrophobic ionizable organic compounds (HIOCs) are among compounds recognized recently as important contaminants of the environment (1). These compounds include both organic acids and bases, which exist in both neutral and ionic forms in aqueous solutions, depending on solution pH:



where HA represents an organic acid and B an organic base. Consideration of both the neutral species and the ionic species is necessary to understand the transport, fate, and effect of these compounds in the environment (2).

Many environmental phenomena involving organic chemicals (e.g., sorption, biological availability, toxicity, etc.) have been related to the octanol-water partition constants of the chemicals. While these relations have been applied extensively for nonpolar compounds (e.g., refs

3 and 4), relatively little is known about their applicability for ionic (amphiphilic) organic compounds. For the distribution of ionic compounds, the counterion must be taken into consideration. In this paper we address the octanol-water distribution of organic bases and organic cations. In related papers (5-8) we address the octanol-water distribution of inorganic ions and organic anions and illustrate the relation of the octanol-water distributions of organic anions to their sorbent-water distributions, for several environmental sorbents.

Application in Environmental Chemistry. The sorption of organic bases to environmental sorbents can be interpreted through four types of mechanisms. (I) hydrophobic partitioning of the neutral organic base:



where the overbar represents a sorbed species; (II) hydrophobic-like sorption of the organic base cation, with counter charge provided by a dominant inorganic counterion such as Cl^- (9):



where $\overline{\text{Y}}$ represents a site or domain for hydrophobic-like sorption; (III) cation exchange of the organic base cation (BH^+) with the dominant inorganic cation on the surface, such as Na^+ (9-17):



where $\overline{\text{X}}$ represents a cation-exchange site; or (IV) formation of a covalent bond between the organic base and the sorbent (18). Evidence for each of these mechanisms exists in the references cited. The results of this study are most directly related to mechanisms I-III.

The octanol-water reference system is of use in understanding the biological effects of organic bases and organic cations as well. Researchers in pharmaceutical and medicinal chemistry (19-21) have reported on the octanol-water distribution of organic bases at different pH values and have discussed the application of the octanol-water reference system to physiological problems.

The scope of this study is confined to the octanol-water distribution of a homologous series of organic bases. Application of these concepts to environmental sorbents and

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