

TROPOSPHERIC LIGHT ALCOHOLS, CARBONYLS, AND ACETONITRILE:
CONCENTRATIONS IN THE SOUTHWESTERN UNITED STATES AND HENRY'S LAW DATA

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Abstract. Aliphatic alcohols ($C_1 - C_n$), aldehydes ($C_1 - C_2$), and ketones ($C_3 - C_n$) have been determined at Tucson, Arizona, and at two rural sites about 40 km distant. Acetonitrile was also measured at the rural sites. The method involved condensation sampling, condensate preconcentration, and gas chromatography. Henry's law coefficients were required for all components and were determined. Mean concentrations in Tucson were higher than those in the rural areas by factors typically between 2 and 8; urban formaldehyde was only slightly elevated. Mean alcohol concentrations ranged from 7.9 ppb (C_1) to 0.12 ppb (C_n) within the city and from 2.6 ppb (C_1) to 0.06 ppb (C_n) at the rural sites. Acetone was found at 12 ppb in the city and 2.8 ppb at the rural sites. Concentrations of butanone were a factor of 5 lower. Acetaldehyde, at 23 ppb (city) and 6.9 ppb (rural), far exceeded formaldehyde concentrations (1.8 ppb in the city, and 1.5 ppb at the rural sites). Acetonitrile was found at the rural sites at a mean concentration of 60 ppt. A dimensionless Henry's law coefficient (mol L^{-1} of liquid/ mol L^{-1} of vapor) was surprisingly similar for the alcohols at 0°C , ranging between 2×10^4 and 3.4×10^4 ($900\text{--}1500 \text{ mol L}^{-1} \text{ atm}^{-1}$); the ketones were a factor of 10 lower. For acetaldehyde the coefficient was 1.7×10^3 ($76 \text{ mol L}^{-1} \text{ atm}^{-1}$) and for acetonitrile 3.7×10^3 ($165 \text{ mol L}^{-1} \text{ atm}^{-1}$). Concentrations of oxygenated organics in the condensates and in precipitation were compared; it was tentatively concluded that concentration differences of the carbonyls were consistent with these species' being produced within the cloud, for example, by aqueous photochemistry.

Introduction

The degradation of atmospheric hydrocarbons by free radicals or ozone results in oxygenated derivatives; such derivatives may also have primary sources, both natural and biogenic [Graedel, 1978]. Their further oxidation can contribute to the production of formaldehyde, carbon monoxide, molecular hydrogen, etc. [Zimmerman et al., 1978; Hanst et al., 1980; Chameides and Cicerone, 1978; Aikin et al., 1982]. The extent to which nonmethane hydrocarbons affect ozone and HO_x radical concentrations is currently a matter of some discussion [e.g., Bottenheim and Strausz, 1980; Brewer et al., 1983].

Aldehydes, ketones, carboxylic acids, alcohols, organic peroxides, and a variety of multifunctionalized organic molecules have been identified in urban air [Graedel, 1978]. Most studies have examined the role of these compounds in the gen-

eration of photochemical smog; little is known about their gaseous concentration in clean air. Difficulties stem from the diversity of oxygenates, their low concentrations, especially in more pristine conditions, and the need for the sampling technique to discriminate between oxygenates and unfunctionalized organic vapors.

The condensation collection method [Farmer and Dawson, 1982] offered promise for such a discrimination. While most light oxygenated organics are not highly soluble (by the criterion of Farmer and Dawson), they are sufficiently more soluble than other atmospheric organics to give preferential incorporation into condensate. In this work, condensation sampling was followed by a preconcentration procedure to give readily detectable levels of the compounds of interest. Henry's law constants at the condensation collection temperature were required and were determined experimentally.

Theory

The theoretical basis of condensate collection has been presented by Farmer and Dawson [1982]; that paper should be consulted for details not given here.

A vertical surface cooled below the ambient dew point collects condensate. If the surface is clean, film condensation occurs; the film drains from the surface and can be analyzed for its aqueous components. A knowledge of the processes of condensation allows atmospheric concentrations to be inferred.

The ambient concentration, $\rho_{A\infty}$ (kg m^{-3}), of trace component A is related to the aqueous concentration, C_A (kg kg^{-1}), by

$$\rho_{A\infty} = C_A \left[\left(\frac{B_A D_v}{B_v D_A} \right) (\rho_{v\infty} - \rho_{vw}) + \frac{\delta}{H_A} \right] \quad (1)$$

where subscript v denotes water vapor, D_A and D_v are molecular diffusion coefficients, B_A and B_v are related to convective boundary thicknesses (given in Farmer and Dawson [1982]), and ρ_{AV} and ρ_{vW} are vapor densities at the collector surface. H_A is a dimensionless Henry's law coefficient for A, defined as

$$H_A = \lim_{C_A \rightarrow 0} (C_A \delta / \rho_{AW}) ;$$

δ is the density of water (1 kg m^{-3} at 4°C).

The form of (1) indicates that two factors relate the atmospheric concentration of A and its condensate concentration. The first product in (1) pertains to transport of vapor to the collector, while the second term is dependent on its aqueous solubility. For compounds of interest to this study, both terms are of comparable magnitude and must be retained. Condensate concentrations are quite low; C_A ranges from 10^{-5} to 10^{-10} ($10 - 10^{-4}$ ppm) depending on atmospheric concentrations and the magnitude of H_A .

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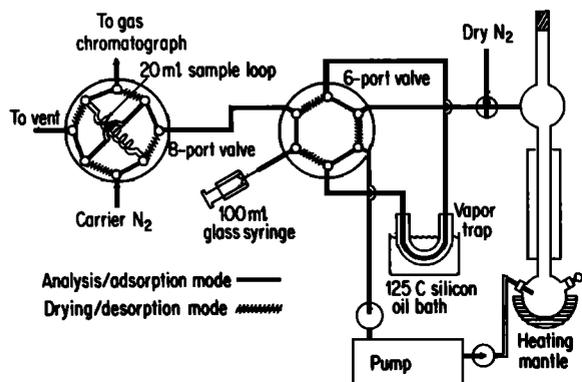


Fig. 1. Diagram of purging and trapping assembly.

Condensates

Method

Condensate was collected using the apparatus and techniques of Farmer and Dawson [1982] with one major difference. In the previous study, mostly highly soluble gases were collected, and for these, aqueous concentration is inversely proportional to collection rate. Farmer and Dawson therefore chose a relatively low rate of 10–15 mL/hour for each of the two collection plates. For the present study, where δ/H_A is not negligible, much higher collection rates can be used; they were typically 15 to 35 mL/hour for each plate when the temperature was kept between 273° and 278°K. Procedures were otherwise as in Farmer and Dawson [1982]. Sixty milliliters of sample were required for analysis of the volatile organics, while another 5 mL were used to determine formaldehyde. Ambient trace vapor levels are, therefore, approximately a 2-hour temporal average.

Collected samples were stored in glass and kept refrigerated prior to analysis. Formaldehyde

analysis was performed within 20 hours of collection, while the other organics were analyzed within 1–3 days. Some rain and hail samples were collected, using a 28-cm diameter glass funnel draining into a 500-mL Erlenmeyer flask. These samples were stored and analyzed in the same manner as the condensate.

Analyses

A Hewlett-Packard 5710-A gas chromatograph, with flame ionization detector and heated 20-mL teflon-lined gas-sampling loop, was used in all work here. Areas under chromatograph peaks were integrated with a Hewlett-Packard 3390-A integrator. The integrator also registered retention times and calculated concentrations from standard runs. A 240 cm \times 0.15 cm ID teflon-lined aluminum column packed with 160 cm of Porapak QS and 80 cm of Porapak S, mesh size 80/100, was used for analysis of the condensate and rain water. A similar column packed with Porapak S was used for some Henry's law determinations. The ultra-high purity nitrogen carrier gas was passed through a cartridge of molecular sieve (5A) and activated charcoal. Columns were conditioned for 2–3 days at 220°C under nitrogen. Optimum performance during analysis was obtained with a temperature program: 90°C for 0.3 min, 16°C min⁻¹ for 6.2 min, and 190°C for 15 min.

Water used for standard solutions was doubly distilled, first from alkaline potassium permanganate; it was then degassed at 98°C for 5 hours with a stream of 99.9995% nitrogen that had passed through a bed of Porapak Q. Water treated in this manner was found to still contain detectable levels of some components present in condensate.

Condensates (and rain) were preconcentrated by microdistillation [Chian et al., 1977]; Figure 1 illustrates the purging and trapping assembly. Fifteen minutes prior to the start of purging, 60 mL of chilled condensate (5–10°C) were added

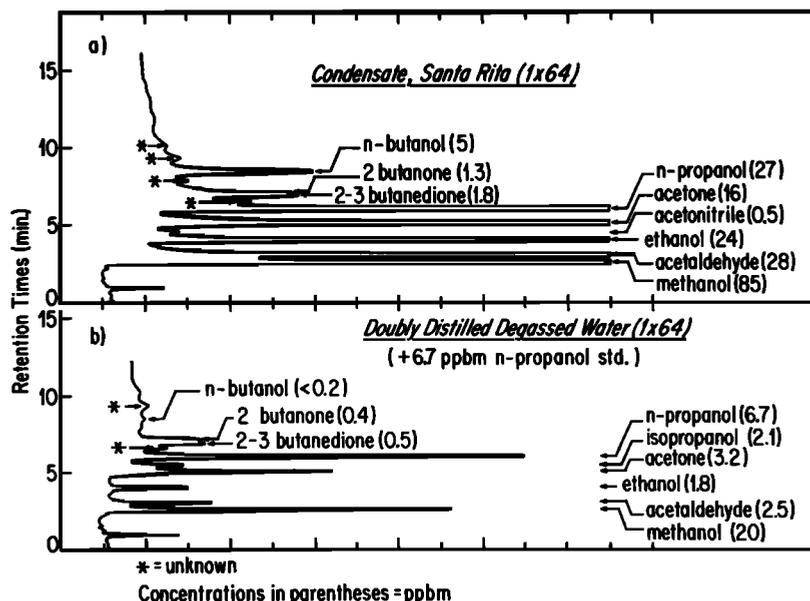


Fig. 2. Chromatograms of condensate sample and degassed distilled water.

TABLE 1. Mean Condensate Concentration, \bar{C} , Standard Deviation of the Concentrations, δC , and Number of Measurements, N, at Each Site

	Tucson		Santa Rita and Mt. Lemmon	
	$\bar{C}(\pm\delta C)$ ppbm	N	$\bar{C}(\pm\delta C)$ ppbm	N
<u>Alcohols</u>				
C_1H_4O	200 (± 70)	17	72 (± 29)	18
C_2H_6O	150 (± 120)	17	19 (± 9)	18
n- C_3H_8O	1.0 (± 0.9)	11		
n- $C_4H_{10}O$	5.7 (± 2.5)	17	3.7 (± 1.8)	18
tert- $C_4H_{10}O$	3.7 (± 1.8)	16		
<u>Ketones</u>				
C_3H_6O	61 (± 27)	17	18 (± 5)	18
C_4H_8O	15 (± 5)	17	3.4 (± 1.0)	18
<u>Aldehydes</u>				
C_1H_2O	200 (± 80)	8	140 (± 81)	27
C_2H_4O	56 (± 28)	17	22 (± 8)	18
<u>Nitrile</u>				
C_2H_3N			0.35 (± 0.1)	18

to the distillation pot, together with a 10- μ L aliquot of the internal standard, n-propanol (160 ppm solution in purified water). The sample was then heated to boiling under nitrogen, while the vapor contents of the still were recirculated at 30 mL/min for 20 min through a valve and porous polymer trap at room temperature with a glass syringe pump. The trapped organics were thermally desorbed (125°C) into the 20-mL sample loop with 25 mL of nitrogen. Standard calibration solutions, of concentration similar to the condensates, underwent the same procedure. The overall efficiency of the trap-and-desorb procedure ranged from 10% for CH_3OH through 20% for CH_3CN , 30-40% for the propyl and butyl alcohols, to 40-45% for the carbonyls, depending on solubility, retention volume, and desorption efficiency.

A typical chromatogram obtained from a condensate sample and a background distilled-water blank are shown in Figure 2. Other than methanol, background impurities in the blank were present at or below 3 $\mu g L^{-1}$, while for methanol the level was larger than this (20 $\mu g L^{-1}$).

In the absence of interfering gas chromatographic peaks or background impurity in the water blank, the lower limit of detection is about 0.1 $\mu g L^{-1}$. At typical condensate concentrations (0.2 - 200 $\mu g L^{-1}$), the precision of this technique is 10-15% (depending on the particular analyte).

Formaldehyde was determined by the Nash [1953] method; bisulfite in large excess is a known interference, but in the low SO_2 conditions here should cause little problem [Klippel and Warneck, 1978]. Atmospheric SO_2 concentrations within Tucson and near the sampling sites here are usually less than 2 ppbv [Dawson and Farmer, 1984].

In Situ Production: Contamination

The film condensation technique is unable to distinguish between those chemical species which are actually collected from the atmosphere and those that result from reactions in the condensate, prior to or during analysis. Simple organic esters (methyl and ethyl acetate) have been shown to undergo no significant hydrolysis during storage and analysis. We have also investigated condensate stability; very little decomposition has been observed over a period of 1 week, provided the condensate is stored in glass and kept chilled (2-4°C). With the exception of the aldehydes, components are stable against oxidation by acidified dichromate and H_2O_2 .

Aqueous Concentrations: Condensate and Rain

Table 1 contains a summary of mean organic levels found in condensate. Data were collected at three different sites: the Tucson site was located on the roof of the Physics and Atmospheric Sciences Building at the University of Arizona, 2 km from downtown Tucson. Mount Lemmon samples were obtained at the crest of the Catalina Mountains (elevation 2.9 km) located 27 km north of Tucson. The Santa Rita site is located in the foothills (elevation 1.3 km) of the Santa Rita Mountains, 52 km south of the University of Arizona campus. Both rural sites must be partially influenced by anthropogenic contamination from the greater Tucson metropolitan area; however, both locations are surrounded by forests of juniper and ponderosa

pine, both gave very similar results and have been lumped together in the tables.

Greater Tucson has a population of about 500,000, with no significant pollution sources other than automobiles. In addition, there are four isolated copper smelters in southern Arizona (the closest 54 km northeast of Tucson), which emit substantial quantities of SO₂. Data were collected during the spring and summer of 1982. Rain (and/or hail) was also collected at the Santa Rita site during condensate collection to allow a comparison between concentrations; this proved to be instructive and will be discussed later.

To convert condensate concentrations to atmospheric levels, Henry's law data under collection conditions are required. A review of the literature revealed that Henry's law coefficients do exist for most compounds of interest here, but they are usually at 298°K, rather than the collector temperature (273°K - 278°K). Calorimetric data were inadequate to permit extrapolation for many components; therefore partition coefficients were determined experimentally.

Henry's Law Coefficients

Method

One-half liter of solution containing 1-4 compounds of interest was placed in a silanized 3-L Erlenmeyer flask equipped with stirbar. These samples were thermostatted in a constant temperature bath (25°C) or an ice/water slurry. Sixty milliliters of displacement gas, at 5 mL/min, displaced head-space gas into the 20-mL gas chromatograph sample loop. No decrease in component concentrations was apparent at displacement flow rates of less than 10 mL/min. Depletion of solute can be neglected in all cases here.

Calibration factors were established by static dilution in a similar container, followed by displacement into the sampling loop. In this case, allowance had to be made for the dilution effect during displacement.

Component concentrations in the vapor equilibrated above these test solutions and in the calibration were similar, but of necessity (since there was no preconcentration step) corresponded to aqueous concentrations much larger than those found in the condensate, or used for that calibration. Typical aqueous concentrations in the determinations of Henry's law constants were 300 mg L⁻¹ for the aliphatic alcohols and 20 mg L⁻¹ for the less soluble aldehydes, ketones, and nitrile. Other investigators [Friant and Suffet, 1979; Kieckbusch and King, 1979] have demonstrated adherence to Henry's law, for similar compounds, at aqueous concentrations below 1000 mg L⁻¹.

Results and Discussion

The partition coefficients are shown in Table 2. Literature values for 298°K are shown to the right of the present data. At 298°K, there is agreement, within experimental error, between the two sets of data.

Table 2 demonstrates that vapor solubilities of the alcohols at 298°K (H_A²⁹⁸) decrease with increasing carbon number. However, the heat liberated on transfer of organic vapor to dilute

solution (ΔH_{tr} = enthalpy of solution at infinite dilution - enthalpy of vaporization of pure organic liquid [Franks and Reid, 1973]) increases with chain length. The solubilities of the aliphatic alcohols (C₁ - C₄) are therefore quite similar at 273°K. Compounds such as acetone and acetonitrile have low intrinsic heats of transfer, and therefore only modestly increased solubility at 273°K. A finite difference form of the Van't Hoff relation can be used to calculate average heats of transfer (ΔH_{tr}) from our measurement of H_A at 298°K and 273°K.

$$\ln \left(\frac{H_A^{273}}{H_A^{298}} \right) = - \frac{\overline{\Delta H_{tr}}}{R} \left(\frac{1}{273} - \frac{1}{298} \right) \quad (2)$$

These results are shown in Table 2 on the right. Comparisons of the calorimetrically determined values, obtained from the literature, with our values obtained from (2), show reasonable agreement in most cases. Discrepancies are undoubtedly due to the relatively small temperature interval investigated, plus experimental error in H_A.

The Henry's law coefficients and their temperature dependencies (via ΔH_{tr}) can now be used with the previously presented condensate concentrations to deduce atmospheric levels using (2).

Atmospheric Concentrations

Table 3 summarizes averaged atmospheric mixing ratios obtained here. Due to the relatively high concentrations of ethanol and acetone in some of the condensates (Table 1), a number of compounds were obscured; e.g., detection of acetonitrile was possible only at the two collection sites outside Tucson. On no occasion were we able to detect acrolein or isopropanol in the condensate samples; these two substances have retention times which are within 0.5 min of acetone. The technique used here is able to resolve all three compounds if present in solution at equal concentration. Glyoxal, (HCO)₂, was not found; it gave a very low response upon purging and chromatography with test solutions. Both 2,3-butanedione and 2-butanone have retention times which are within 0.2 min of each other. On many occasions, a broadening of the peak centered at 7.0 min indicated that the diketone may have been present in the condensate; however, the area of this peak is reported as resulting solely from 2-butanone. Tertiary butanol was identified and quantitated in Tucson, but was not detected outside town. Formaldehyde mixing ratios at or above 1 ppbv were found at all three sites but were highest in the city; urban and biogenic contributions cannot be separated. All other substances exhibited significantly lower mixing ratios when sampled outside Tucson.

Discussion

With the exception of formaldehyde, none of the organic vapors investigated in this study have been extensively studied in both urban and rural environments. Table 3 contains a summary of the measurements made by other investigators. Noteworthy are the sparse data on the aliphatic alcohols.

TABLE 2. Dimensionless Partition Coefficients (mol L⁻¹ in liquid/mol L⁻¹ in vapor) and Enthalpies of Transfer Found in This Study and by Others

	Partition Coefficients (Dimensionless)				Enthalpies of Transfer (kcal/mol)			
	Experimental		Literature		This Study		Literature	
	This Study		Literature		From Eq. (2)		Literature	
	H _A ²⁷³ (×10 ³)	H _A ²⁹⁸ (×10 ³)	H _A ²⁹⁸ (×10 ³)	Refer- ence	$\overline{\Delta H}_{tr}$	ΔH_{tr}^{298}	ΔH_{tr}^{273}	Reference
<u>Alcohols</u>								
C ₁ H ₄ O	25 (±3)	5.5 (±0.5)	5.5	5	9.8	10.7	11.4	1, 2, 8
C ₂ H ₆ O	33 (±2)	4.7 (±0.2)	4.8	5	13	12.5	13.7	1, 2, 8
n-C ₃ H ₈ O	30 (±4)	3.3 (±0.1)	3.6	5	14	13.8	15.3	1, 2, 8
iso-C ₃ H ₈ O	28 (±3)	3.1 (±0.1)			14	14.0	15.5	1, 2, 8
n-C ₄ H ₁₀ O	26 (±1)	3.1 (±0.2)	2.9	4	14	14.8	16.6	1, 2, 8
sec-C ₄ H ₁₀ O	23 (±3)	2.7 (±0.1)			14	15.0	17.2	1, 2, 8
tert-C ₄ H ₁₀ O	20 (±3)	1.7 (±0.2)			16	15.4	17.9	1, 2, 8
iso-C ₄ H ₁₀ O		2.5 (±0.2)				14.4	16.2	1, 2, 8
<u>Ketones</u>								
C ₃ H ₆ O	2.5 (±0.1)	0.63 (±0.03)	0.67	4	8.9	9.7		6, 7
C ₄ H ₈ O	2.3 (±0.1)	0.43 (±0.02)	0.53	4	11			
C ₄ H ₈ O ₂		1.4 (±0.2)						
<u>Aldehydes</u>								
C ₂ H ₄ O	1.7 (±0.1)	0.31 (±0.02)	0.38	4	11	10.3		6, 3
C ₃ H ₄ O	0.80(±0.09)	0.18 (±0.1)			9.7			
C ₃ H ₆ O			0.33	4				
<u>Nitriles</u>								
C ₂ H ₃ N	3.7 (±0.4)	1.2 (±0.1)			7.3			
C ₃ H ₅ N						7.5		6

- Alexander and Hill [1969]
- Arnett et al. [1969]
- Bell and Clunie [1951]
- Buttery et al. [1969]

- Buttery et al. [1971]
- National Research Council [1929]
- Kister and Waldman [1958]
- Polák and Benson [1971]

Alcohols

Cavanagh et al. [1969] found methanol, ethanol, and normal butanol at Barrow, Alaska, and concluded that they were produced by starch-fermenting bacteria in Arctic tundra. Photochemistry of methane and ethylene [Graedel, 1978; Meagher and Heicklen, 1976], combustion [Bellar and Sigsby, 1970; Hoff and Kapsalopoulou, 1964], anthropogenic emissions [Hoshika et al., 1981], and perhaps the oceans [Zafiriou, 1975] have also been suggested as potential sources of atmospheric alcohols. Dominant atmospheric sinks should be reaction with hydroxyl radical. Lifetimes against attack by OH (at a mean concentration of 10⁶ cm⁻³) range from 11 days for methanol [Overend and Paraskevopoulos, 1978] to 5 days for normal butanol [Graedel, 1978]. Wet removal, even for methanol, should be comparatively slow.

In contrast to the results of Cavanagh et al. [1969], concentrations here decreased rapidly with carbon number, C₁ - C₄. Levels of n-propanol were surprisingly low; it and tertiary butanol

could be detected only in the city. The city was clearly a source of methanol and ethanol, but not of n-butanol; the concentration ratio, urban to rural, was greater for ethanol than for all other species measured. The city source was apparently not vaporization of gasoline; none of the major suppliers in Tucson admitted to adding ethanol in 1982.

A statistical test was performed for difference between day and nighttime concentrations (see Table 4). Of the alcohols, only the butanols showed a significant difference, and then only for the Tucson data; nighttime values were higher. Since butanols are sometimes used as gasoline additives, these results suggest that gasoline evaporation after the evening "rush hour" and lower vertical mixing rates produce the larger nighttime values within the city. The absence of other measurable diurnal differences, city or rural, is not surprising for these long-lived species; it does not allow us to distinguish between primary emission or photochemical production. Both emissions and radical-mediated production and loss could easily have similar diurnal variation.

TABLE 3. Atmospheric Concentrations of Light Organics Observed in This Study and by Other Workers

	This Study				Other Investigators			
	Tucson		Santa Rita and Mt. Lemmon		Urban Ref.	Rural Ref.	Remote	Ref.
	Feb.-Sept. 1982	N	Aug.-Sept. 1982	N	ppbv	ppbv	ppbv	
	<u>Alcohols</u>							
C ₁ H ₄ O	7.9 (±2.6)	17	2.6 (±1.1)	18			0.4-1.2	3
C ₂ H ₆ O	3.3 (±2.0)	17	0.40 (±0.17)	18			0.4-1.2	3
n-C ₃ H ₈ O	0.02 (±0.01)	11*						
n-C ₄ H ₁₀ O	0.12 (±0.06)	17	0.06 (±0.03)	18			50-130	3
tert-C ₄ H ₁₀ O	0.12 (±0.07)	16						
	<u>Ketones</u>							
C ₃ H ₆ O	12 (±4)	17	2.8 (±0.8)	18	≈20	10	1-3	7
C ₄ H ₈ O	2.8 (±1.3)	17	0.50 (±0.16)	18	0-13	4		0.1
	<u>Aldehydes</u>							
C ₁ H ₂ O	1.8 (±0.6)	8	1.5 (±1.0)	27	0.7-5	6	0.4-3.8	6,11
C ₂ H ₄ O	23 (±12)	17	6.9 (±2.5)	18	1-35	4	1-2	2
							0.1-0.6	9,11
							0.02	8
	<u>Nitrile</u>							
C ₂ H ₃ N			0.06 (±0.02)	18			<7	1
							>0.01	5

δC is the standard deviation of the concentration data, N the number of measurements.

*Toluene used as internal standard in early 1982

1. Becker and Ionescu [1982]
2. Breeding et al. [1973]
3. Cavanah et al. [1969]
4. Grosjean [1982]
5. Henschen and Arnold [1981]
6. Neitzert and Seiler [1981]
7. Robinson et al. [1973]
8. Singh and Hanst [1981]
9. Zafiriou et al. [1980]
10. Johansson [1978]
11. Lowe et al. [1981]

Carbonyls

The carbonyls also exhibited much higher concentrations in the city than at the rural locations. City concentration of acetaldehyde was particularly high, and one can safely assume that it resulted primarily from automobile emissions, while the rural levels reflected secondary photochemical production. The acetaldehyde/formaldehyde ratio was much larger than usually found for urban areas. No definitive explanation can be offered, and neither determination seems to be in error. The formaldehyde concentration in Tucson in 1982 is comparable to that found in 1980 using different techniques (55 measurements giving a mean of 1.2 ppb, unpublished). One must always consider the possibility of another compound co-eluting with acetaldehyde, though the likelihood of this seems vanishingly small. The chromatographic identification follows condensation and

distillation steps which closely define an acceptable range of solubility in water. No other light organics have similar retention time on Porapak and comparable water solubility. The large acetaldehyde/formaldehyde ratio must go unexplained.

As expected, acetone was present in fairly high concentration.

The carbonyls, other than acetone, showed significant diurnal differences at the rural sites; a daytime maximum was found. Only formaldehyde may have shown the same trend in Tucson (Table 4). The diurnal changes could result from photochemistry, precursor transport, or dilution by nighttime drainage. Since the alcohols did not show a similar trend, these observations argue that transport and drainage were not major factors. It seems likely, therefore, that the alcohol concentrations are dominated by primary emissions and the carbonyls by photochemical production.

TABLE 4. Parametric Test of Difference Between the Means of Daytime and Nighttime Mixing Ratios, \bar{C}_d and \bar{C}_n

Compound	$\bar{C}_d \pm \delta C_d$	$\bar{C}_n \pm \delta C_n$	N_d	N_n	Probability of Difference Between \bar{C}_d and \bar{C}_n
<u>Tucson</u>					
tert-butanol	0.087 ± 0.073	0.162 ± 0.039	10	6	0.96
n-butanol	0.096 ± 0.053	0.160 ± 0.054	11	6	0.97
formaldehyde	2.25 ± 0.25	1.53 ± 0.56	5	3	0.91
<u>Nonurban Locations (Mt. Lemmon and Santa Rita Experimental Range)</u>					
n-butanol	0.072 ± 0.033	0.057 ± 0.028	8	10	0.65
formaldehyde	2.0 ± 1.4	1.1 ± 0.5	13	14	0.96
acetaldehyde	8.3 ± 2.2	5.8 ± 2.2	8	10	0.96
2-butanone	0.59 ± 0.16	0.42 ± 0.13	8	10	0.97
acetone	3.2 ± 0.8	2.8 ± 0.7	8	10	0.70

δC is a standard deviation; N_d and N_n are the number of day and night measurements, respectively.

Acetonitrile

A brief note on the acetonitrile data has already been published [Snider and Dawson, 1984]. Expected surface concentrations [Brasseur et al., 1983] lie between 10 and 20 ppt. Our measurements are therefore compatible with this background concentration upon which are superimposed some contributions from Tucson itself.

Precipitation Samples

Thunderstorms occurred between September 9 and 11, 1982, at the Santa Rita site during the collection of condensate, allowing samples of rain and hail to be obtained. The processes of liquid water production and precipitation in clouds are vastly more complex than the processes of condensation on the collector surfaces used here. Nevertheless, there are similarities, since gas/liquid partitioning is involved at some stage in both cases. (We shall assume that vapor/liquid interactions, as opposed to vapor/ice interactions dominate.) Not surprisingly, the precipitation samples contained the same constituents as found in the condensates. The actual concentrations are not of great interest here since they depend, inter alia, on cloud liquid-water content, cloud base height, evaporation, and so on. Only ratios of concentrations, precipitation to condensate, will be discussed; the data are shown in Table 5. In general, carbonyl compounds exhibited enhanced levels in the precipitation, whereas alcohols and CH_3CN were greatly depleted. This difference appears to be based more on functionality than solubility; the alcohols, as a group, all have fairly large solubilities, but CH_3CN is a poorly soluble gas. Though all the carbonyls were enhanced, HCHO is more soluble than the alcohols, while the other carbonyls are less soluble than CH_3CN . Partition is not therefore the explanation. Similarly, different vertical distributions resulting from varia-

tions in solubility cannot be accepted either. Thunderstorms were occurring; the atmosphere was convectively unstable and should have been well mixed. None of the components is highly soluble; in a cloud, all should be partitioned primarily into the gas phase. As a result, the vertical distributions of all components are likely to have been similar. There is no evidence for some sort of special interaction between any of the compounds here and ice, and so we shall not suggest one. Rather, we shall suggest another explanation of these intriguing trends, which must, at this time, be considered highly speculative.

The data are most easily explained if either the alcohols and CH_3CN are being destroyed within the cloud, or carbonyls are being produced. Alcohols and CH_3CN are well-used solvents, all relatively stable against aqueous oxidation. The concentration ratio (precipitation/condensate) for these compounds is virtually identical within experimental error; it is surely highly unlikely that they would all be destroyed by a similar amount. Much more likely is that their concentration ratio is that of a substance not undergoing any chemical change within the cloud. If that is the case, then perhaps the carbonyl compounds, formaldehyde, acetaldehyde, acetone, and 2-butanone are produced by in-cloud processes. At this time, this appears to the authors to be the most likely, though speculative, explanation. Aqueous phase photochemical oxidations have recently been discussed by Chameides and Davis [1982] and Graedel and Weschler [1981].

Conclusions

This study was undertaken to examine the usefulness of the film condensation method for sampling moderately soluble organic vapors. Many of these substances are thought to be intermediates in the degradation of atmospheric methane and

TABLE 5. Mean Aqueous Concentrations of Precipitation and Condensate and Their Ratio at Santa Rita

	Mean Condensate Concentration C_c ppbm	Mean Precipitation Concentration C_p ppbm	Number of Measurements	C_p/C_c
<u>Alcohols</u>				
C_1H_4O	56	22	4	0.39 (± 0.05)
C_2H_6O	15	4.6	4	0.31 (± 0.03)
n- C_3H_8O				
n- $C_4H_{10}O$	3.2	0.89	4	0.28 (± 0.09)
<u>Ketones</u>				
C_3H_6O	16	23	4	1.4 (± 0.4)
C_4H_8O	2.1	4.6	4	2.2 (± 0.7)
<u>Aldehydes</u>				
C_1H_2O	130	220	5	1.7 (± 0.6)
C_2H_4O	15.5	66	4	4.3 (± 1.7)
<u>Nitrile</u>				
C_2H_3N	0.43	0.18	4	0.42 (± 0.05)

nonmethane hydrocarbons, others originate directly from anthropogenic and biogenic emissions. This technique, when combined with a condensate pre-concentration step, is capable of detecting these particular organic vapors at sub-ppb levels in the atmosphere. Henry's law coefficients at collector temperature are required and were determined.

Previous measurements of some of the components, e.g., the alcohols and acetonitrile are very sparse.

Sampling in Tucson, Arizona, and at two rural sites demonstrated that the light alcohols and carbonyls have some sources within that urban area. Alcohol levels showed little diurnal variation; carbonyls exhibited a definite daytime maximum at the nonurban sites.

Acetonitrile was detected at the two rural sites at concentrations which are consistent with those observed in the lower stratosphere by other workers. Acetonitrile is rather poorly soluble, and thus its wet removal from the atmosphere should be small.

Concentrations of oxygenated organics in precipitation and in condensates were compared. It was tentatively concluded that the light alcohols and acetonitrile remained relatively unreactive within cloud water, while concentrations of the carbonyls were consistent with their being produced within the cloud, for example, by aqueous photochemistry.

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