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Measurements of C_2–C_5 Hydrocarbons Over the North Atlantic

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Latitudinal distributions of ethane, propane, propene, and acetylene in air over the Atlantic from 48°N to 4°S are reported. In addition, measurements of saturated and unsaturated hydrocarbons (C_2–C_5) at low latitudes and from 55°N to 80°N are presented. The mixing ratios of ethane, propane, and acetylene were found to vary systematically between a few tenths of a ppb and a few ppb. The alkene and higher alkane (C_4 and C_5) mixing ratios were found to be in the ppt range. The data are discussed with respect to the source distributions and atmospheric lifetimes of the different hydrocarbons.

INTRODUCTION

Light hydrocarbons have been shown to be present in surface air at mixing ratios from a few tenths to a few ppb [cf. *Robinson,* 1978]. Although their mixing ratios are much lower than that of methane, it is conceivable that the nonmethane hydrocarbons (NMHC) contribute to the photochemical reactions in nonpolluted air in a significant way because their reaction with OH proceeds much faster than that of CH_4. To test this hypothesis, survey measurements of the background distribution of NMHC are required. For that purpose we have developed a gaschromatographic method which enables the determination of C_2 to C_5 hydrocarbons at mixing ratios in the lower ppt range from grab samples of 0.5 to 2 dm^3 (STP). As a first step towards a survey we have collected 39 air samples during two cruises of the research vessel F. S. *Meteor* (cruises 51 and 52) in 1979 and analyzed them in the laboratory. The results of these measurements are presented in this paper.

EXPERIMENTAL

The air samples were collected in evacuated stainless steel spheres (0.5–2 dm^3) with metal bellow valves. These containers were carefully cleaned and pretreated to avoid sample contamination or losses during sample storage (the conditioning of the sample storage containers has been described by *Ehhalt et al.* [1976]). The blank values caused by these evacuated and pretreated containers were below the detection limit of the gaschromatographic analysis, i.e., the blank values were below 5 ppt for all the hydrocarbons except C_2H_2 (<20 ppt) and i-C_5H_{12} (<10 ppt). The samples were stable for several months without detectable changes of the concentrations of the trace gases under investigation.

The samples were analyzed with a Packard 419 gaschromatograph equipped with a flame ionization detector. Two different procedures for the enrichment of the light hydrocarbons and two different columns were employed. The first series of measurements was done with a Porapak R packed column (100–120 mesh, column: 7 feet × 1/8"). Air samples of up to 0.5 dm^3 (STP) were injected while the column was kept at −80°C. At this temperature the hydrocarbons (with the exception of CH_4) were enriched at the head of the separation column ('on-column enrichment'). Then the column temperature was increased from −80°C to 120°C with a heating rate of 15°C min^{-1}. With 0.5 dm^3 air samples this method allowed the determination of C_2H_6, C_2H_2, C_3H_8, and C_3H_6 down to mixing ratios of ≈ 30 ppt. It was used to analyze samples taken in January and February 1979 between 48°N and 4°S (cruise 51, part I and II).

Other samples, collected in early May 1979 between 3°N and 4°S and in August and September between 55°N and 81°N (cruise 51, part V and cruise 52), were analyzed by enrichment of the hydrocarbons on a precolumn packed with Spherosil and Carbosieve at ≈ −100°C and subsequent separation on a 6 m × 0.8 mm column packed with Spherosil XOB 075 in a temperature program from −90°C up to 70°C. This improved method allowed the enrichment from sample volumes as large as 2 dm^3 (STP). The determination of C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6, i-C_4H_{10}, n-C_4H_{10}, i-C_5H_{12} and n-C_5H_{12} was possible with detection limits of approximately 5–20 ppt depending on the type of compound and the available sample amount.

The measurements were calibrated with standards prepared by static dilution of the hydrocarbons in synthetic air. Three dilution steps were employed to obtain standards with mixing ratios between 0.1 ppbv and 5 ppbv. The precision of the analyses was 5–10% or 5–20 ppt, whichever is larger; the errors depended to some extent on the type of compound.

RESULTS

The samples reported here were collected on board of the F.S. *Meteor* (January and February 1979, cruise 51, part I and II; May, cruise 51, part V; August–September, cruise 52). Sampling conditions (e.g., sampling positions on the ship and direction and velocity of relative air motion) were carefully chosen to minimize all possible contaminations from the ship itself. In addition, these samples were analyzed for CO and H_2, and samples which showed elevated CO or H_2 concentrations were rejected. Although shipboard sampling is generally connected with serious contamination problems, these problems are considerably reduced for simple grab sampling, because the sampling procedure itself is simple, fast (takes only a few seconds), and flexible with respect to the place of the sampling. This enables a careful selection of the sampling conditions, thus considerably reducing the contamination problem.

The observed latitudinal variations of C_2H_6, C_2H_2, C_3H_8, and C_3H_6 from 48°N to 4°S are presented in Figures 1–3. These samples were taken during January and February 1979 (F.S. *Meteor,* cruise 51, part I and II). The results from the analysis of samples collected between 4°S and 3°N in early May 1979 are listed in Table 1 (F.S. *Meteor,* cruise 51, part V). The hydrocarbon mixing ratios in air samples from the second voyage of the F.S. *Meteor* in August and September

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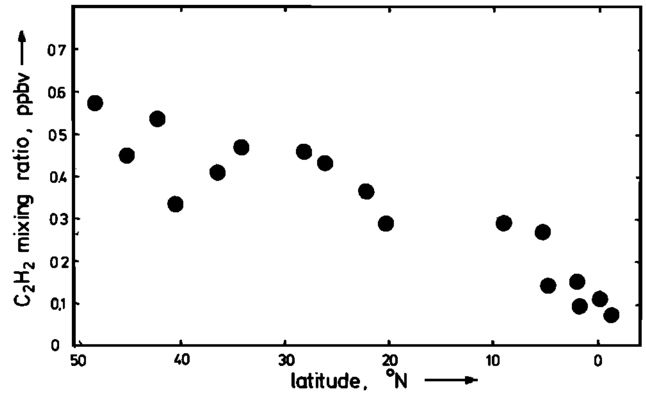

Fig. 1. Latitudinal variation of the C_2H_2 mixing ratio (Atlantic, January and February 1979).

1979 into the North Atlantic and Barent Sea are presented in Table 2 (cruise 52). The tracks of these parts of the 1979 *Meteor* cruises are shown in Figure 4.

DISCUSSION

Before we attempt to discuss the individual distributions of the measured NMHC, it is appropriate to point out a few features which are common to all NMHC data. These are related to the fact that the dominant sink of all NMHC is the reaction with OH; moreover, that the reactions are relatively fast, resulting in atmospheric lifetimes of a few months to a few hours for the NMHC considered here (cf. Table 3). Thus their chemical lifetimes are short or at least comparable to the timescales of tropospheric transport, and transport will not be able to smooth out the inhomogeneities in the respective distributions of the (surface) sources or the variations in the sink distribution. We have to expect a good deal of variability in the data. Some of that variability, especially that connected with the OH sink term, will be systematic. The production of OH depends on the product of the solar UV flux, atmospheric ozone, and water vapor concentration. Consequently, the OH concentration will show strong vertical and latitudinal gradients as well as diurnal gradients and at higher latitudes will also show seasonal variations. These variations should cause corresponding variations in the mixing ratios of the NMHC, the response depending on the lifetime. The possibility of such systematic variations should be borne in mind when data collected at different locations and in different seasons are compared or when inferences about the global averages are drawn from the data.

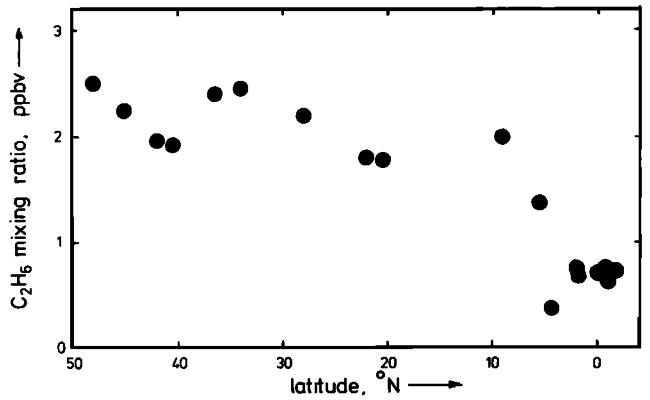

Fig. 2. Latitudinal variation of the C_2H_6 mixing ratio (Atlantic, January and February 1979).

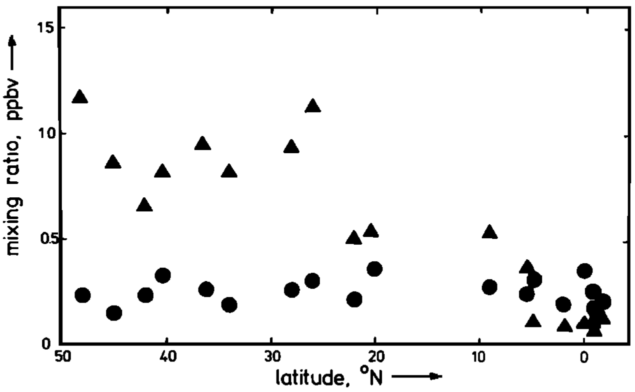

Fig. 3. Latitudinal variation of the mixing ratios of C_3H_8 (triangles) and C_3H_6 (circles) (Atlantic, January and February 1979).

Acetylene

Acetylene is the longest lived NMHC. Its average global chemical lifetime is nearly 4 months (cf. Table 3). It should show a relatively low variability. Indeed, judging from figure 1, the latitudinal distribution of acetylene over the Atlantic during January and February 1979 shows a more or less linear decrease with latitude from 0.6 ppb at 50°N to 0.1 ppb at the equator. The superimposed deviations from linearity are small; there is an indication of a steeper gradient between 10°N and the equator.

The only other data on the latitudinal distribution of C_2H_2 are measurements by R. A. Rasmussen published by *Robinson* [1978]. The bulk of the data was obtained between October 26 and November 18, 1976, over the Pacific aboard the NASA Convair 990 aircraft *Galileo II* and therefore was collected well above the earth's surface. These data show lower mixing ratios, 0.3 ppb at 50°N and 0.05 ppb at the equator, but a similar more or less linear decrease again by about a factor of 6 in the northern hemisphere. The differences in mixing ratio are easily explained by the fact that C_2H_2 shows a vertical gradient with altitude in the troposphere (J. Rudolph et al., unpublished manuscript, 1981). In addition, longitudinal changes are expected, since the sources of C_2H_2 are located on the continents. C_2H_2 is emitted by fossil fuel burning (internal combustion engines, oil fired heating, etc.). Significant biological sources of acetylene are not known at present. Thus its source distribution should be very closely related to that of energy production. The latitudinal distribution of Figure 1 is, between 48°N and 4°S, fully compatible with that source distribution and a sink distribution determined by the meridional distribution of OH.

Ethane

C_2H_6 is the most abundant of the light NMHC. Its latitudinal distribution over the Atlantic during January and February is shown in Figure 2. Compared to C_2H_2, it seems to show a more stepwise decrease with a steeper gradient between 10°N and the equator. The equatorial mixing ratio is about a factor of three lower than at midlatitudes.

C_2H_6 data collected during October and November 1976 over the Pacific aboard the NASA Convair 990 aircraft and published by *Robinson* [1978] have a poor latitudinal resolu-

TABLE 1. Hydrocarbon Volume Mixing Ratios (ppb) Over the Equatorial Atlantic

Time, GMT	Date	Longitude	Latitude	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	C_2H_4	C_3H_6	C_2H_2
1010	May 8, 1979	22°W	01°20′S	1.0	0.1_7	0.1_1	0.02_5	0.03_5	0.02_0	0.4_5	0.1_1	0.1_0
1030	May 1, 1979	26°30′W	04°07′S	1.0	0.1	0.0_7	0.02_0	0.02_5	0.01_5	0.5_0	0.0_9	0.0_7
1405	May 5, 1979	22°W	01°44′N	0.7_3	0.0_6	0.0_3	0.01_5	0.01_0	0.00_5	0.1_0	0.0_9	0.1_8
1545	May 7, 1979	22°W	00°00′	0.8_6	0.1_3	0.00_8	0.02_0		0.02_0	0.0_8	0.1_6	0.2_8
1620	May 3, 1979	22°W	00°08′N	0.8_9	0.1_3	0.0_5	0.02_0	0.01_5	0.01	0.1_5	0.1_4	0.0_8
1815	May 4, 1979	22°W	02°52′N	0.9_0	0.2_6	0.1_8	0.04_0	0.06_0	0.02_5	0.2_5	0.1_4	0.1_8

To show any diurnal variation, the data are listed with respect to the daytime.

tion but are consistent with a steep decrease at low northern latitudes. The same pattern is shown by surface data from the cruise of the USNS *Hayes* in March 1974 over the Pacific [*Robinson*, 1978]. The absolute mixing ratios, however, are lower by about a factor of 2–0.8 ppb, at midlatitudes and 0.3 ppb at the equator for both measurement series over the Pacific, than our data over the Atlantic. Provided that the seasonal and secular variations of the C_2H_6 mixing ratios can be neglected, the absence of significant differences in the C_2H_6 mixing ratios at different altitudes over the Pacific would indicate that the vertical gradient of C_2H_6 over the Pacific is small and that the difference to the present data must be caused by longitudinal gradients possibly introduced by the source distribution. Additional data on the latitudinal distribution of C_2H_6 have been published by *Singh et al.* [1979]. Most of the comparable data were collected on coastal stations of the eastern Atlantic between September 15 and October 30, 1977. They show scattered mixing ratios between 1 and 3 ppb at northern midlatitudes and between 0.5 to 1 ppb at the equator. Although they are not inconsistent with the present measurements and exhibit a general decrease towards the equator, the older data do not allow the identification of the actual shape of the latitudinal C_2H_6 distribution in the northern hemisphere.

The average global lifetime of C_2H_6 is about 2 months and thus slightly shorter than that of C_2H_2 (cf. Table 3). Thus, if the source distributions of C_2H_2 and C_2H_6 were similar, C_2H_6 should show a slightly steeper decrease than C_2H_2. This is not the case; namely, between 50°N and 10°N C_2H_6 decreases significantly slower than C_2H_2. Thus the present measurements clearly demand a C_2H_6 source or sink distribution different from that of C_2H_2. Indeed, in addition to sources in the industrialized latitude belt, C_2H_6 is also released by natural gas and oil fields which reach as far south as 30°–10°N. A further source of C_2H_6 is probably the ocean itself. As shown by *Lamontagne et al.* [1974], ocean water contains dissolved C_2H_6. The concentrations were found to be higher by about a factor of 5 than the equilibrium concentration in water, as calculated from the measured mixing ratio of C_2H_6 in the atmosphere and the solubility data given by *McAuliffe* [1966]. Thus the oceans should release C_2H_6 at a relatively low but uniform rate.

Propane

The latitudinal distribution of C_3H_8 over the North Atlantic is shown in Figure 3. We could not find any other published data on its latitudinal distribution. The latitudinal variation of C_3H_8 presented in Figure 3 shows a decrease in its mixing ratio between 30° and 20°N that is much steeper than found for C_2H_2 or C_2H_6. Yet C_3H_8 is expected to have similar sources to those for C_2H_6, including a contribution from the oceans. However, the atmospheric removal of C_3H_8 by reaction with OH is much faster than that of C_2H_6 (cf. Table 3). Thus the C_3H_8 distribution responds to the higher OH concentrations in the tropics with a decrease more rapid than that of C_2H_6. As a consequence the equatorial mixing ratios of C_3H_8 are more than a factor of 10 lower than those at midlatitudes, compared to the factor of 3 found for C_2H_6.

Propene

Figure 3 also shows the latitudinal distribution of C_3H_6 over the North Atlantic. In constrast to the previously discussed hydrocarbons, there is no systematic latitudinal gradient. The mixing ratio varies around 0.2 ppb at all latitudes. Since the atmospheric lifetime of C_3H_6 is quite short (at low latitudes about 10 hours (cf. Table 3)) horizontal transport from sources on the continents cannot be the explanation for the observed C_3H_6 concentrations over the middle of the ocean. It must have local sources, i.e., emission from the ocean surface. Moreover, the strength of this source is required to increase towards lower latitudes in order to maintain a constant mixing ratio against the increasing removal through reaction with OH. There is one piece of information which points in that direction. *Lamontagne et al.* [1974] reported a broad maximum in the concentration of

TABLE 2. Hydrocarbon Volume Mixing Ratios (ppb) Over the North Atlantic and the Barents Sea

Latitude	Longitude	Date	Time, GMT	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	C_2H_4	C_3H_6	C_2H_2
55°N	5°E	August 8	1300	3.3	2.5	1.3	0.47	0.41	0.49	0.40	0.17	0.40
63.5°N	3°E	August 12	1200	1.9	0.37	1.10	0.09	1.3	5.3	0.20	0.10	0.30
69°N	1°W	August 15	1830	1.5	0.37	0.17	0.11	0.07	0.11	0.09	0.14	0.30
75°N	1°W	August 16	2130	1.5	0.30	0.07_5	0.05	0.09	0.04	0.06	0.11	0.20
81°N	9°W	August 19	1315	1.5	0.15	0.02_5	0.08	0.02	0.02	0.01_5	0.05_5	0.11
79°N	9°E	August 20	2340	1.6	0.45	0.16	0.11	0.03	0.04	0.15	0.10	0.24
78°N	12°E	August 24	2020	1.2	0.13	0.02_5	0.02	0.03	0.01_5	0.10	0.01_5	0.12
75°N	22°E	August 27	1510	1.0	0.15	0.03	0.02	0.03	0.05_5	0.04	0.04	0.10
73°N	27°E	August 30	1150	1.0	0.23	0.06	0.03_5	0.04	0.02_5	0.10	0.10	0.10
72°N	15°E	August 31	2250	1.3	0.28	0.09	0.02	0.06	0.02	0.36	0.17	0.08
71°N	30°E	September 1	2230	1.3	0.32	0.25	0.04_5	0.14	0.03_5	0.51	0.20	0.12

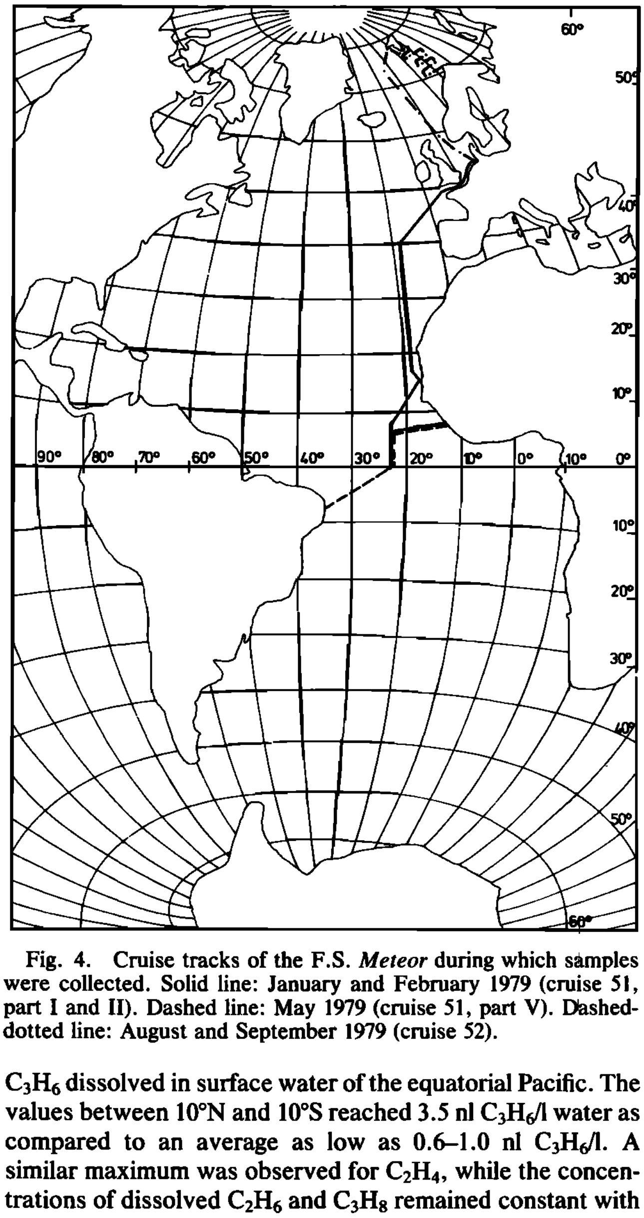

Fig. 4. Cruise tracks of the F.S. *Meteor* during which samples were collected. Solid line: January and February 1979 (cruise 51, part I and II). Dashed line: May 1979 (cruise 51, part V). Dashed-dotted line: August and September 1979 (cruise 52).

C_3H_6 dissolved in surface water of the equatorial Pacific. The values between 10°N and 10°S reached 3.5 nl C_3H_6/l water as compared to an average as low as 0.6–1.0 nl C_3H_6/l. A similar maximum was observed for C_2H_4, while the concentrations of dissolved C_2H_6 and C_3H_8 remained constant with latitude at 0.2 nl/l and 0.3 nl/l, respectively. Because of the large supersaturations the release rates are directly proportional to the concentration of dissolved C_3H_6; thus the equatorial Pacific is expected to have a three times higher C_3H_6 release than the higher latitudes. A similar increase in the tropical Atlantic would explain the atmospheric C_3H_6 mixing ratios presented in Figure 3.

Other NMHC

During two further cruises (F. S. *Meteor*, cruise 51, part V, and cruise 52) other NMHC, namely C_2H_4, $n-C_4H_{10}$, $i-C_4H_{10}$, $n-C_5H_{12}$, and $i-C_5H_{12}$, were measured over the northern and the equatorial Atlantic. The data are summarized in Tables 1 and 2. These hydrocarbons are rather shortlived, with lifetimes of the order of a few days or less (cf. Table 3). Their presence in the maritime atmosphere hence can only be explained by local release of these NMHC from the ocean itself. Tables 1 and 2 show some covariance between the mixing ratios of the various NMHC. However, since the data were not collected in a systematic way, it is not possible to correlate the observed mixing ratios with physical or biological parameters. Insolation intensity, biological activity of the surface water, etc. could cause systematic spatial and temporal variations in the release rates of the NMHC. Moreover, the removal rate, dominated by OH, varies with the solar UV flux and thus shows a strong diurnal cycle. This forces a diurnal variation in those NMHC with lifetimes less than a few days. Indeed, the data listed in Table 1 are not inconsistent with a diurnal variation for most of the short-lived NMHC.

The presented informations of the short-lived NMHCs suggest that the ocean should present a source of these gases. To test whether the oceanic source of light hydrocarbons can maintain the observed hydrocarbon mixing ratios in the atmosphere against photochemical removal, the oceanic source strength should be compared with the atmospheric destruction. This can be done for the area between ≈ 70–77°N and ≈ 10°E–5°W, for which *Swinnerton and Lamontagne* [1974] reported measurements of light hydrocarbons in ocean water. Some of our measurements of hydrocarbons in air (Table 3) agree nearly exactly in season and location with these data.

To estimate the flux from the ocean into the atmosphere, we use the formulation of *Liss and Slater* [1974] for transport across the air-sea interface, the solubility data of *McAuliffe* [1966], the oceanic hydrocarbon measurements by *Swinnerton and Lamontagne* [1974], and our own atmospheric data. The resulting emission rates are:

for C_2H_6:

$$3 \times 10^{-11}\ \mathrm{g\ cm^{-2}h^{-1}}$$

for C_3H_8:

$$4 \times 10^{-11}\ \mathrm{g\ cm^{-2}h^{-1}}$$

for C_2H_4:

$$6 \times 10^{-11}\ \mathrm{g\ cm^{-2}h^{-1}}$$

for C_3H_6:

$$5 \times 10^{-11}\ \mathrm{g\ cm^{-2}h^{-1}}$$

TABLE 3. Atmospheric Lifetimes of Light Hydrocarbons

			Lifetime,* d	
Compound	k_{OH}, cm^3 mole^{-1} s^{-1}	k_{O_3}, cm^3 mol^{-1} s^{-1}	Low Latitudes	Global
C_2H_6†	2.9×10^{-13}		20	61
C_3H_8‡	1.5×10^{-12}		4	12
n-C_4H_{10}‡	2.5×10^{-12}		2	7
i-C_4H_{10}‡	2.4×10^{-12}		2.1	7.5
n-C_5H_{12}‡	3.7×10^{-12}		1.5	4.8
i-C_5H_{12}‡	4.6×10^{-12}		1.2	3.9
C_2H_4§	8.1×10^{-12}	1.67×10^{-18}	0.7	1.8
C_3H_4‖	1.5×10^{-11}	1.02×10^{-17}	0.3	0.6
C_2H_2¶	1.6×10^{-13}		35	110

* Lifetimes are based on an OH radical concentration of 2×10^6 mol/cm^3 (24 h average) for low latitudes and 6.5×10^5 mol/cm^3 for global average respectively [*Volz et al.*, 1979], and on an ozone mixing ratio of 30 ppb [*Routhier et al.*, 1980].

†k_{OH}: *Howard and Evenson* [1976].

‡k_{OH}: *Greiner* [1970].

§k_{OH}: *Atkinson et al.* [1977]; k_{O_3}: *Herron and Huie* [1974].

‖k_{OH}: *Davis* [1976]; k_{O_3}: *Herron and Huie* [1974].

¶k_{OH}: *Davis et al.* [1975].

To obtain the atmospheric destruction rate, we have to integrate over the full tropospheric altitude range. For that purpose, vertical concentration profiles of the NMHC, OH, and O_3 at ≈ 70°N are required.

For our calculations we adopted the shape of the vertical profiles calculatd for some light hydrocarbons by *Chameides and Cicerone* [1978]. For the alkenes which they had not calculated, we used a steeper scale height proportional to the square root of the lifetimes. This is only a rough approximation, but it turns out that the destruction rates decrease very rapidly with altitude, since the temperature dependent rate constants and the NMHC and the OH concentrations decrease with altitude, and thus the shape of the vertical profile at higher altitudes is of little importance. The OH profile was taken from *Volz et al.* [1981] and the O_3 concentration from *Routhier et al.* [1980].

The resulting atmospheric removal rates for this area (70–77°N, 10°E–5°W) are:

for C_2H_6:

$$4 \times 10^{-11}\ \mathrm{g\ cm^{-2}h^{-1}}$$

for C_3H_8:

$$5 \times 10^{-11}\ \mathrm{g\ cm^{-2}h^{-1}}$$

for C_2H_4:

$$9 \times 10^{-11}\ \mathrm{g\ cm^{-2}h^{-1}}$$

for C_3H_6:

$$1 \times 10^{-10}\mathrm{g\ cm^{-2}h^{-1}}$$

Both the atmospheric removal and the oceanic emissions rates have considerable uncertainties (variations in oceanic and atmospheric hydrocarbon concentrations, transfer resistance for the air-sea exchange, atmospheric OH concentrations, the shape of the vertical NMHC profiles, etc.). Nevertheless, the comparison of the source and sink strengths for the light hydrocarbons indicates that the observed hydrocarbon mixing ratios in the marine atmosphere at these far northern latitudes may indeed be due to oceanic emissions.

No measurements of light hydrocarbons in ocean water in the equatorial Atlantic are known to us. The oceanic hydrocarbon concentrations which are necessary to balance the photochemical removal in the atmosphere over the equatorial Atlantic are estimated to be 6 nl/l for C_2H_6, 1.5 nl/l for C_3H_8, 8 nl/l for C_2H_4, and 4 nl/l for C_3H_6.

Lamontagne et al. [1974] and *Swinnerton and Lamontagne* [1974] have reported hydrocarbon concentrations for the equatorial Pacific of 0.22–0.31 nl/l for C_2H_6, 0.33–0.47 nl/l for C_3H_8, 3.9–5.7 nl/l for C_2H_4, and 2.2–3.4 nl/l for C_3H_6. If similar values hold for the equatorial Atlantic, the observed atmospheric mixing ratios of the short-lived alkenes could well be explained by oceanic emissions, while for longer-lived ethane, long-range transport should contribute significantly.

CONCLUSIONS

The observed latitudinal distribution of light nonmethane hydrocarbons over the Atlantic indicate that the observed species (with the exception of acetylene) are at least partly emitted by the ocean. Due to their high reactivity, the alkenes (C_2H_4 and C_3H_6) are the most important of these compounds. From the measured mixing ratios of the light NMHC and their reaction rate constants with OH (cf. Table 3) it can be seen that their contribution to the photochemistry in the marine atmosphere is about 80% that of methane at ≈ 60°N and about 50% that of methane at low latitudes over the Atlantic. This indicates that these light hydrocarbons indeed do contribute significantly to photochemical reactions in unpolluted air. Up to now the known data on light NMHC are not extensive enough to allow any global inferences. Consequently, for a quantitative understanding of the importance of the oceans as a source for hydrocarbons—and their influence on the marine photochemistry—further measurements are necessary. Data from the southern hemisphere, vertical profiles for the more reactive hydrocarbons, seasonal variations, and measurements of dissolved hydrocarbons in ocean water are lacking. Individually, most of the hydrocarbons we investigated have only a slight influence on the photochemistry in the marine atmosphere, but the cumulated effect of all NMHC may be considerable. Our measurements, by far, do not cover the complete range of hydrocarbons. There may be many other species present at mixing ratios below ppb, as is indicated by the fact that *Eichmann et al.* [1979, 1980] found small but significant amounts of C_9–C_{17} *n*-alkanes in clean air masses of marine origin.

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