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Abstract

The role of organic molecules in multiphase atmospheric systems is illustrated by two examples. The first draws attention to the possible role of an organic surface film on aerosol particles; the second discusses the role of "in cloud" chemistry in the formation of HCOOH and CH_3COOH from light alkanes. Vertical and meridional distributions of C_2 to C_5 hydrocarbons are presented which underline their importance at the midlatitudes of the northern hemisphere. An attempt is made to quantify the global emissions of individual light non-methane hydrocarbons, and the various sources of $\text{C}_2 - \text{C}_5$ hydrocarbons are briefly discussed.

Introduction

Organic compounds are present in all phases of the atmospheric chemical system. They constitute a major class of gaseous trace species, they occur in precipitation, and they form a significant fraction of the atmospheric aerosol.

Obviously, there must exist heterogeneous chemical pathways which interconnect the organic molecules in those three "phases". In fact there is a number of them and it is not possible to cover them all. Instead we will concentrate on two examples, where multiphase chemical reactions of organic molecules seem to be of more general importance. In the second part of the paper we will investigate the question of mass balance: Are there enough organic molecules around to make them globally important? Here also it is not possible to cover all classes of organic molecules, and we will restrict the discussion to the light hydrocarbons, the class of organic molecules which is most abundant in the atmosphere.

Multiphase chemistry of organic molecules

One of the most interesting interactions of organic molecules is based on the fact that higher organic molecules form monolayers which have lower free surface energies than most other substances. Thus they tend to remain and accumulate on surfaces (Somorjai, 1982). Aerosol particles from many locations have been reported to contain organic matter (Ketseridis and Eichmann, 1978; Winkler, 1983) on the order of 10 %. A fair fraction of that organic matter is insoluble in water (Winkler, 1983), and we may expect that much of that fraction is concentrated on the surface of the particles. Indeed, such an organic surface layer was already considered by Junge and Scheich (1969), and such considerations led Graedel and Weschler (1981) to publish the aerosol model which is shown in Figure 1.

Fig. 1 Schematic model of atmospheric aerosol particles (after Graedel and Weschler, 1981).

The model particle consists of an insoluble core. This core is surrounded by a layer of water which may account for 30 % or more of the particles weight, depending on the relative humidity. This layer, actually an aqueous solution, contains significant amounts of dissolved inorganic and organic compounds. It is covered by a surface film of organic material consisting of polar molecules. These can be visualized as fatty acids, alcohols etc. with their polar functional groups (indicated by the circles) oriented towards the liquid core. The non polar part made up by an aliphatic chain of C- and H-atoms is oriented towards the surface. Clearly such a veneer of oriented organic molecules - if it could be maintained for an appreciable fraction of the lifetime of the aerosol - would determine the surface properties of the aerosol particles. It would influence the sticking probability of gaseous molecules to the surface of the aerosol. The hydrophobic ends would influence the wettability of the aerosol surface. The film would act as a barrier for certain molecules, e.g. H_2O . And finally the C-H chains would react selectively with other molecules. For example, attack by hydroxyl radicals and subsequent oxygen attachment could lead to highly reactive surface sites of peroxy groups.

Despite its potential importance the existence of that organic surface layer, although plausible on general grounds, is by no means established. The techniques for its identification had not been available. It is therefore all the more important to know that with the "Lamma Sonde" a technique has become available which allows just that (van Grieken and Adams, 1983). There is hope now, to determine what kind of aerosol particles, if any, carry such an organic surface film and to obtain a clue of what its nature may be.

Our next example is from the field of cloud and precipitation chemistry. Precipitation has been found to contain formaldehyde (CH_2O) and acetaldehyde, CH_3CHO - CH_2O at a concentration of 0.05 to 0.15 mg/l (Klippe1 and Warneck, 1978; Thompson, 1980; Lowe et al., 1981; Lowe and Schmidt, 1983); CH_3CHO about a factor of five less.

Formic acid, HCOOH , and acetic acid, CH_3COOH , have been reported at even higher concentrations and that at background stations. Galloway et al. (1982) published precipitation measurements which give an average concentration of 0.7 mg/l for HCOOH and 0.27 mg/l for CH_3COOH for four background stations. Moreover Keene et al. (1983) point out that in one of the stations, Katherine, Australia, these two acids contribute 63 % of the total acidity. The authors conclude that organic acids may play an important part in regulating the acidity in the precipitation of remote continental areas. The available sets of measurements of CH_2O , CH_3CHO , HCOOH and CH_3COOH are rather limited and not sufficient to draw general conclusions.

Nevertheless they indicate one feature which is rather interesting. Whereas the amounts of CH_2O and CH_3CHO found in precipitation can easily be explained by the gas phase production of these gases from light hydrocarbons, this becomes difficult when we turn to the corresponding acids. The quoted organic acid concentrations in rain are quite high. To illustrate that, we assume for the moment that they be globally representative. Assuming further a global precipitation rate of 100 cm/yr these concentrations would correspond to a global wet deposition of HCOOH of about

$$300 \times 10^{12} \text{ g/yr,}$$

and a wet deposition of CH_3COOH of about

$$100 \times 10^{12} \text{ g/yr.}$$

These are quite large figures. And though as global average, they may be quite uncertain, they indicate that the deposition of formic and acetic acids is much higher than the presently known surface emissions. Unless the precipita-

tion measurements are wrong both substances must be generated within the atmosphere and - judging from their large amounts - they must be generated from molecules with a large global source strength.

It also appears that there are just not enough olefins around, which through reaction with O_3 and via the Criegee intermediate are known to yield $HCOOH$ and CH_3COOH . Thus one must look for additional precursors for the production of the organic acids. And in the following we will investigate, whether or not the alkanes might serve that purpose.

For clarity we will do it for the simplest molecule that would allow the production of acetic acid, namely ethane, C_2H_6 . The reaction sequence is described in the following (cf. Aikin et al., 1980). The oxidation of C_2H_6 begins with a reaction with the OH -radical which abstracts an H -atom and leaves an ethyl radical.

Because of the large abundance of O_2 , the next step the addition of O_2 to form the ethylperoxi radical is very fast. There is no chance for competing reactions. The ethyl peroxi radical is polar and should be water soluble a fact which we indicate by underlining. It is also relatively longlived, since the subsequent reaction with HO_2 giving ethyl hydroperoxide or, with NO giving ethoxy radicals are both relatively slow.

Depending on the HO_2 and NO concentrations $\text{CH}_3\text{CH}_2\text{OO}$ could live between a few hundred to a few thousand seconds, enough time to allow collisions with aerosol particle surfaces or with cloud droplets in a cloud. Thus heterogeneous reactions are possible, and in a cloud even probable.

The products, $\text{CH}_3\text{CH}_2\text{OOH}$ and $\text{CH}_3\text{CH}_2\text{O}$, of the gas phase reaction are also water soluble, and $\text{CH}_3\text{CH}_2\text{OOH}$ is longlived enough to make heterogeneous removal possible, especially in a cloud. The ethoxy radical is shortlived, with a lifetime of a few milli-seconds only; it will react within the gas phase.

Unimolecular decay of $\text{CH}_3\text{CH}_2\text{O}$ gives formaldehyde, its reaction with O_2 yields acetaldehyde. At groundlevel the rate of the latter reaction is about 6 times faster. We also note that in this case another peroxy radical is formed: HO_2 . The resulting CH_2O and CH_3CHO are the longest lived intermediate products of the ethane oxidation. They live about 10 hours against gas phase reaction with OH or against photolysis and are water soluble; heterogeneous reactions are possible and very likely in a cloud. The methyl radical formed in reaction (5) reacts further to form also CH_2O .

The gas phase reactions will eventually degrade H_2CO and CH_3CHO to CO_2 and H_2O . Acetaldehyde can further react to eventually form peroxyacetyl nitrate, PAN. The sequence contains 3 steps.

An abstraction of the H-atom by OH to form an acetyl radical is followed by the fast addition of O_2 to form the peroxyacetyl radical which reacts with NO_2 to form PAN. The dissociation to NO_2 and the peroxyacetyl radical depends strongly on temperature. At 20 °C the lifetime of PAN against unimolecular decay is a few hours.

Up to this point in the reaction sequence the various reaction products have been: Peroxy radicals, HO_2 , CH_3O_2 , $\text{CH}_3\text{CH}_2\text{O}_2$, and CH_3COO_2 , the peroxides H_2O_2 (not explicitly mentioned) and $\text{CH}_3\text{O}_2\text{H}$, the aldehydes, H_2CO and CH_3CHO , and finally PAN. All these substances are water soluble and long lived enough to be incorporated into cloud droplets when produced within the cloud. Then the presence of ethane (and other light hydrocarbons) will add substantially to the balance of HO_2 and H_2O_2 in a cloud. Moreover it adds a whole host of higher radicals and peroxides to the wet chemistry which had so far not been considered (cf. Chameides, 1983).

But up to this point neither formic nor acetic acid have been formed in the reaction sequence. There is a good reason for this: the gas phase production of formic and acetic acid from C_2H_6 is not very likely. One can construct gas phase pathways leading to those acids, but they do not seem to proceed with high efficiencies. There is, however, a good chance that aqueous phase reactions do convert CH_2O to $HCOOH$ and CH_3CHO to CH_3COOH . Thus both acids can be formed from C_2H_6 oxidation inside a cloud.

In the following we will outline the process for H_2CO . H_2CO is highly soluble in water. Upon dissolution it readily forms a hydrate, methylene glycol $H_2C(OH)_2$ (at room temperature 99.9 % of the dissolved H_2CO are in the form of $H_2C(OH)_2$). There are several pathways how methylene glycol can convert to formic acid. One has been suggested by Graedel and Weschler (1981). It relies on the reaction with dissolved OH, which during daytime is likely to be present at high concentrations in cloud water (Chameides and Davis, 1982; see also Chameides and Davis, 1983; Chameides, 1983). The OH-radical abstracts an hydrogen atom, the resulting radical $CH(OH)_2$ reacts with dissolved O_2 to form $HCOOH$ and a HO_2 radical (Chameides and Davis, 1983).

Another possibility is the reaction of $H_2C(OH)_2$ with H_2O_2 also known to be present in cloud and precipitation water, both, from experiment and theory (cf. Chameides and Davis, 1982). The direct reaction appears to be slow. In any case there is at least one efficient reaction in aqueous phase to convert CH_2O via methylene glycol to formic acid. With a simple estimate we can convince ourselves that this path may be of global importance. Assuming OH concentration in the range of 6×10^7 to $6 \times 10^8 \text{ cm}^{-3}$ in the liquid gas phase as estimated by Chameides and Davis (1982) and the reaction rate constant of $2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ quoted by Chameides and Davis (1983) for $OH + CH_2(OH)_2$, one obtains a lifetime of 500 to 5000 sec for CH_2O in cloud droplets. With an effective Bunsen solu-

bility of 4×10^5 for CH_2O with respect to dissolved $\text{H}_2\text{C}(\text{OH})_2$ and a liquid water content of 1 g/m^3 in the cloud one obtains a lifetime for CH_2O in the cloud between 1.5×10^3 and 1.5×10^4 sec, about a factor of 3 to 20 shorter than in outside air. Since clouds make up about 10 % of the tropospheric volume, it is quite conceivable that a significant fraction, on the order of 10 %, of the tropospheric CH_2O is converted to HCOOH via cloud chemistry. Some of the HCOOH will be rained out with the forming precipitation. Another fraction of the HCOOH will be oxidized to CO_2 and H_2O by OH in the cloud droplets. However, since most of the clouds evaporate, much of the thus formed HCOOH will end up in aerosol particles or evaporate also to form gaseous HCOOH , whose final fate is gas phase oxidation to H_2O and CO_2 .

A quite analogous process exists for the conversion of CH_3CHO to CH_3COOH . It should be slower because CH_3HCO is much less soluble than H_2CO . Thus gas phase production of CH_3COOH may still be required to explain the high concentration in rain observed by Galloway et al. (1982).

In the case of acetic acid, there is of course also the possibility of the uptake of PAN by cloud droplets and its subsequent hydrolysis to acetate and nitrate. But PAN is even less soluble in water than CH_3CHO and its hydrolysis is slow. The time constant for hydrolysis is about 1 h (at 22 °C and a pH of 5.6 (Lee et al., 1983)). Though possible, this process appears too inefficient to produce the large concentration of acetic acid observed in background precipitation.

As far as CH_3COOH is concerned we are left with a twofold problem. Firstly, the presently known conversion processes of hydrocarbons to CH_3COOH are too inefficient to produce the large CH_3COOH concentrations in rain reported, even including multiphase reactions. Secondly, the global emissions of hydrocarbons appear to be insufficient to balance the deposition of CH_3COOH (see table 2 below).

Our second example showed how gas phase chemistry and wet phase chemistry interplay to oxidize an alkane to formic and acetic acid. The gas phase oxidation of C_2H_6 worked to produce soluble organic compounds: the aldehydes. The aqueous phase chemistry completed the oxidation to acids. We also saw that this chemistry which occurs in clouds might be of global importance.

The atmospheric distribution of non methane hydrocarbons

What we have shown so far is that organic molecules are potentially important for atmospheric multiphase chemistry. The actual importance of organic molecules depends of course on the concentrations of the gaseous precursors in the atmosphere. And this point we would like to address next. There is a great variety of organic molecules in the atmosphere and not all that much is known about their distributions. Thus we will concentrate on the light nonmethane hydrocarbons $C_2 - C_5$, NMHC, which are known best. These molecules also make up the bulk of the hydrocarbons in the atmosphere. This means that we learn very little about the precursors of the organic molecules which are important for aerosol particles because these must have much higher C numbers to remain condensed. But we will have a fair picture of the most important precursors for the formation of acetic and formic acid and peroxy radicals.

We will first take a look at the vertical distribution of light hydrocarbons. Vertical profiles of $C_1 - C_5$ hydrocarbons are summarized in Figure 2 (Rudolph et al., 1982a). They were obtained using grab sampling aboard an aircraft and subsequent analysis by gas chromatography in the laboratory (Rudolph et al., 1982a). The triangular symbols represent samples collected over northern Germany during October and November 1979; the dots represent samples collected over Southern France in June 1979. Of course, the data points do show some scatter. This is to be expected for trace gases whose atmospheric lifetime ranges from a few months, C_2H_2 , C_2H_6 , to a week or so for the alkanes C_3H_8 ,

Fig. 2 Vertical profiles of hydrocarbons over Europe (cf. Rudolph et al., 1982a). The triangles represent samples collected during October and November 1979 over the Eifel mountains, Germany, 52° N latitude; the dots represent samples collected in June 1979 over Southern France, 43° N.

C_4H_{10} , C_5H_{12} , and a day for the olefins C_2H_4 , C_3H_6 , and whose sources are highly local. Nevertheless, all these gases present clearly a common picture: Higher mixing ratios, nearly constant with altitude, in the boundary layer, a sharp dropoff at the boundary layer which was at 800 mb pressure or 2 km altitude, a slower decrease above that altitude to a background value which seems to be reached by about 400 mb or 7.2 km altitude. This points to strong sources for these gases at the continental surface which in this case must be clearly industrial. The source strengths for the various gases as expressed by the mixing ratio enhancement in the boundary layer are quite different. For CH_4 the enhancement amounts to 100 ppb, for CO to 150 ppb, for C_2H_6 only 1 ppb for C_2H_2 0.7 ppb and for the C_2H_4 only 0.3 ppb. The only exception is CH_3Cl whose gradient is inverted indicating the nonexistence of a surface source in this region. We also note that the absolute mixing ratios are quite different. They range from 1600 ppb for CH_4 to 0.2 ppb for $n-C_5H_{12}$. The mixing ratios of hydrocarbons show a rather regular pattern: a decrease from low C numbers to high C numbers. For straight chain alkanes this is illustrated in Figure 3. This bar graph shows the mixing ratio of alkanes beginning from CH_4 (C=1), C_2H_6 (C=2) to n-decane (C=10) for two stations. One, indicated by crosshatched bars, is a remote mountain station in Germany, which at the time of sampling was above the boundary layer and should be as close to background conditions as you can get in middle Europe. The big jump in concentration between CH_4 and C_2H_6 is followed by a more or less regular decrease of a factor 1.5 or so with increasing carbon number.

Next we investigate the latitudinal distribution of light hydrocarbons. This is done with the help of samples taken during a number of cruises of the research vessel F.S. Meteor in the Atlantic. The results for C_2H_6 are shown in Figure 4 (Rudolph and Ehhalt, 1981, Rudolph et al., 1982b). The cruise data are supplemented by a few data from Antarctica indicated by the open triangles. The scatter within each cruise is relatively small. But the data

Fig. 3 Distribution of the atmospheric mixing ratio of straight chain alkanes from two locations. Schauinsland is a mountain station (1200 m above sea level) in the Black Forest area, Germany; the other station refers to a small wooded area close to Jülich, Germany.

Fig. 4 Latitudinal distribution of C_2H_6 in surface air over the Atlantic. The dates of the ship cruises are indicated by different symbols. The open triangles represent samples from the Ross and Faraday base, Antarctica, during December 1980 and January 1981 (after Rudolph et al., 1982b).

for the March cruise are significantly higher than the others. In principle this could be assigned to a systematic seasonal variation of the hydrocarbon mixing ratio. Such a seasonal variation would not be unexpected and has been observed for C_3H_8 , for example (Singh and Salas, 1982). However, as we shall see, the other hydrocarbons do not show this difference which seems to exclude that explanation.

Despite this scatter the data show a clear and systematic latitudinal variation: There are lower mixing ratios of about 1 ppb at high latitudes, the values increase towards midlatitudes. A broad maximum is reached between 50° and 10° N with mixing ratios between 2 and 4 ppb. South of 10° N the mixing ratios show a very rapid decrease towards the equator reaching values below 0.5 ppb. The southern hemisphere exhibits uniformly low C_2H_6 mixing ratios between 0.5 and 1 ppb.

This behaviour clearly indicates strong C_2H_6 sources at northern midlatitudes. It also confirms the expected strong sinks in the tropics, which are due to the elevated OH concentrations there. We also note that the mixing ratio maximum is shifted to the lower latitudes, i.e. the areas where most of the crude oil and natural gas is produced rather than to the latitudes where most of the industries and heaviest car traffic are located. This becomes even more evident when we consider the latitudinal distribution of C_3H_8 (Figure 5) which exhibits less scatter and therefore a much better defined maximum of nearly 1 ppb between 40° and 20° N. The rest of the latitudinal distribution of C_3H_8 is also quite similar to that of C_2H_6 , with low values in all of the southern hemisphere and low values at polar latitudes. A quite similar behavior was also found for butane.

Our next example is the distribution of C_2H_2 (Figure 6), a gas which is mostly produced by incomplete combustion. On the first glance it looks quite similar to those of the light alkanes: low values in the southern hemisphere, a strong, well

Fig. 5 Latitudinal distribution of the C_3H_8 in surface air over the Atlantic.

The dates of the ship cruises are indicated by different symbols.

The open triangles represent samples from the Ross and Faraday base, Antarctica, during December 1980 and January 1981 (after Rudolph et al., 1982b).

Fig. 6 Latitudinal distribution of C_2H_2 in surface air over the Atlantic. The dates of the ship cruises are indicated by different symbols. The open triangles represent samples from the Ross and Faraday base, Antarctica, during December 1980 and January 1981 (after Rudolph et al., 1982b).

defined maximum at northern midlatitudes. On closer inspection, however, we detect a few differences. The increase in mixing ratio from the equator to midlatitudes is less abrupt, starting at the equator and reaching the maximum at 30° N instead of 10° or 20° N as for C_2H_6 . In addition the maximum of the C_2H_2 mixing ratio straddles 40° N instead of 30° in the case of the alkanes. That behaviour is quite plausible. As mentioned C_2H_2 is emitted during incomplete combustion of fossil fuel - mostly from automobiles. Its latitudinal distribution, therefore, reflects the consumption of fossil fuel rather than the production of fossil fuel as is the case for C_2H_6 . And the consumption of fossil fuel takes place mostly in the industrial countries around 40° N.

So we see that the latitudinal distribution affords a first glimpse on the nature of the sources of the light hydrocarbons. This becomes even more apparent when we consider the latitudinal distribution of propylene, C_3H_6 (Figure 7). The data for propylene scatter somewhat more strongly and show less systematic variation than the alkanes do, so for clarity we show a running average of the data as indicated by the curve. The vertical bars indicate the mean standard deviation. Clearly C_3H_6 shows a different latitudinal distribution than C_2H_2 or the light alkanes: Between 60° N and nearly 10° S the C_3H_6 mixing ratios over the Atlantic Ocean are more or less constant with latitude. What is even more surprising, these mixing ratios are relatively high, 0.15 ppb, very close to what we found over continental Europe. On the other hand, C_3H_6 is highly reactive and thus shortlived. Its lifetime is about 0.6 days in midlatitudes and 0.3 days in the tropics. Therefore transport from continental sources cannot explain the C_3H_6 mixing ratios found over the ocean, and a local i.e. oceanic source of C_3H_6 seems required. This is indeed the case. Measurements by Swinnerton and Lamontagne (1974) and Lamontagne et al. (1974) have shown that the ocean is highly supersaturated in C_3H_6 by about a factor of 100. In fact the observed mixing ratios of C_3H_6 can be fully explained by oceanic emissions (Rudolph and Ehhalt, 1981). The same is true for ethylene.

Fig. 7 Running average of the latitudinal distribution of C_3H_6 in surface air over the Atlantic using a 15° averaging interval. The curve is based on data from the same cruises as listed in Figure 4. The vertical bars indicate the mean standard deviation.

As interesting and informative as the NMHC measurements over the ocean are, they only provide one dimension in the required global distribution. What one really would like is a picture of the NMHC in at least 2 dimensions, namely latitude and altitude. In April and May, 1980 we had the opportunity to participate in the "Stratoz II" flight of the French Caravelle research aircraft. The flight track is shown in Figure 8. It took about 3 weeks to complete it. The plane landed about every 3000 km which allowed to take vertical profiles during the approach to the airports, whose positions are indicated by the dots. Because of the expected pollution close to the airports no samples were taken below 800 mb. The meridional distribution shown in the following are divided into a southbound leg leading from Greenland to Puntas Arenas, and a northbound flight segment from Puntas Arenas to Paris.

Since it is not possible to present all of the data, only a few selected examples are shown. The other NMHC cross sections will be published by Rudolph et al. (1984). Figure 9 gives the meridional distribution of ethane during this flight. For clarity the figure does not contain the individual data points, but rather the isolines of constant mixing ratio interpolated between them. The meridional distribution of C_2H_6 shows a number of characteristic features which are repeated in the distributions of the other trace gases as well. As in the measurements over the ocean surface we note a mean latitudinal gradient now at all altitudes, the mixing ratio decreasing as we go from mid-north latitudes to the equator and into the southern hemisphere. We also have generally a clear vertical decrease of mixing ratio with altitude. There is however one conspicuous exception. There is a definite cell of maximum mixing ratios around 50° N latitude and about 10 km altitude in the southbound flight. Such a maximum - although much less pronounced - is also present over the tropics during the northbound flight. The maximum at 50° N causes a very steep vertical gradient towards the tropopause. It also influences the isolines

Fig. 8 Flight track of the STRAT0Z II experiment.

Fig. 9 Latitude-altitude cross section of the C_2H_6 mixing ratio obtained during STRATOZ II. The contours of the constant mixing ratio are given in ppb.

further south in the sense that they run more or less trapezoidal with the exception of some wiggles probably superimposed by air mass movements. These are the regular distribution features which we can extract from Figure 9. At the same time we note substantial variability which is expressed in the bends and folds of the lines of constant mixing ratio. They are caused by large scale advection. We further note that the south and northbound cross sections differ significantly indicating at least temporary zonal variations. For C_2H_6 this is not very conspicuous, but generally the northbound leg over the African Coast shows lower mixing ratios than the southbound leg.

The same features are visible for ethylene (Figure 10): latitudinal gradient, vertical gradient, a cell of maximum mixing ratios at 10 km altitude at 50° N. Here this maximum is even more surprising, since C_2H_4 is shortlived and not likely to be transported over large distances. We also note how the high mixing ratios in the planetary boundary layer cause a convex bulge pushing the 1 ppb isoline upward to 3 km altitude at midlatitudes. C_2H_2 is the only case where the cell of maximum mixing ratios is so weak that it cannot be traced with certainty. But mixing ratios of 0.3 ppb, i.e. as high as in the boundary layer, are certainly found at 50° N and 10 km altitude (Figure 11). Here, the upwelling in the tropics is also clearly visible; we further note an upward thrust of higher mixing ratios over the equator.

All the above mentioned features are also found for propane (Figure 12) and for isobutane (Figure 13). Indeed they are present for all the NMHC (C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , C_3H_6 , nC_4H_{10} , iC_4H_{10} , nC_5H_{12} , iC_5H_{12}) which we measured, as well as for CO (Schmidt et al., 1982).

Whereas the latitudinal or vertical gradients can easily be explained by surface sources, the cell of maximum mixing ratios at 10 km altitude, 50° N presents somewhat of a puzzle. The common appearance in all NMHC cross sections points to a common mechanism.

Fig. 10 Latitude-altitude cross section of the C_2H_4 mixing ratio obtained during STRAT0Z II. The contours of constant mixing ratio are given in ppb.

Fig. 11 Latitude-altitude cross section of the C_2H_6 mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppb.

Fig. 12 Latitude-altitude cross section of the C_3H_8 mixing ratio obtained during STRAT0Z II. The contours of constant mixing ratio are given in ppb.

Fig. 13 Latitude-altitude cross section of $i\text{-C}_4\text{H}_{10}$ mixing ratio obtained during STRATOZ II. The contours of constant mixing ratio are given in ppt.

It is quite tempting to assume that the maximum of NMHC mixing ratios observed at 10 km altitude and 50° N latitude is caused by exhaust emissions of commercial jet aircraft. The flight path of the Caravelle aircraft followed over large parts the trans-Atlantic flight pattern of that day. It is even conceivable that the Caravelle was following another plane relatively closely and thus encountering relatively high levels of pollution. And this was indeed our first thought when we saw these data. There is, however, a serious inconsistency in the explanation: When we calculate the ratio of excess CO to excess NMHC ($C_2 - C_5$) in the maximum, the ratio of carbon atoms, C_{CO}/C_{NMHC} amounts to about 5. A jet engine however emits very few NMHC in the $C_2 - C_5$ range (cf. Figure 14). Most of the exhausted hydrocarbons have carbon numbers above 7, and the ratio of CO to NMHC ($C_2 - C_5$) is much larger namely about 100 which seems to rule out a large contribution by jet exhaust. On the other hand most of the NMHC emitted by a gasoline engine are in the range $C_2 - C_9$ (cf. Figure 14) and the carbon ratio of CO to the NMHC with $C_2 - C_5$ is much lower namely about 10. This value is also observed in the boundary layer as a whole. The NMHC observed in the maximum show a pattern more consistent with boundary layer air.

If this checks out there must be rather fast transport processes to carry the observed high concentrations of olefins to these altitudes. For example an extended front with high reaching thunderstorms which could pump boundary layer air quickly to altitudes close to the tropopause. We have not yet backed up this possibility by trajectory analysis.

The current explanation of the maximum introduces another point. The two dimensional cross sections given above represent a more or less instantaneous snapshot of the atmospheric distribution of NMHC. Rather shortlived meteorological processes could have influenced them. To extract an average meridional distribution from them can be misleading.

Fig. 14 The distribution of hydrocarbons in the exhaust of a gasoline engine, a diesel engine and a jet engine, under specified operating conditions. Hydrocarbons with the same carbon number are lumped together. The full portion of the bars for the gasoline engine indicates the fraction of aromatic compounds.

We will need quite a few more of these profiles to obtain a good global average. At the same time, the observations indicate the potential value of measurements of NMHC concentrations as traces of atmospheric transport processes. What are then the conclusions on the NMHC distributions which will stand up? We still can say with certainty that the highest mixing ratios of NMHC are found in the planetary boundary layer, i.e. close to the earth's surface and at the midlatitudes of the northern hemisphere. We can also state that there is a general decrease in mixing ratio with altitude which is the steeper the shorterlived the hydrocarbon compound is. But occasionally relatively high mixing ratios of NMHC in the middle and upper troposphere of the northern midlatitudes must be expected. The mixing ratios in the tropics and in the southern hemisphere are much lower than in the northern hemisphere, except for C_2H_4 and C_3H_6 or others with a large oceanic surface source.

That is to say that much of the multiphase atmospheric chemistry of NMHC must go on in northern midlatitudes, where most of the current investigations take place. It seems important to keep this bias in mind.

Sources of NMHC

We have repeatedly talked about the sources of NMHC, and in this last chapter we will attempt to quantify these sources. This is difficult. There are regional studies which provide detailed budgets for the individual hydrocarbons, for Los Angeles for example or for Sydney. But there are no detailed global estimates. All published estimates of global HC emissions are bulk numbers giving only the run of all hydrocarbons (cf. NAS, 1976; Duce et al., 1982). As a consequence we are forced to prepare a detailed budget without precedents. This is not an easy task, and the uncertainties in such an estimate are large.

The uncertainties in the CH_4 budget for example are about a factor of 2. This, despite the fact that CH_4 with global emissions totalling about 500×10^{12} g/yr is the most important and the best investigated of the HC.

The estimates for the $\text{C}_2 - \text{C}_5$ hydrocarbons which we will present must be much more uncertain, and one may question the rationality behind such crude estimates. Our excuse is that we have to start somewhere and that these crude estimates still allow us to determine which sources appear more important globally and should therefore be investigated with highest priority. Table 1 summarizes the emission estimates for the $\text{C}_2 - \text{C}_5$ hydrocarbons. For comparison we have added some estimates of a few aromatic compounds and of the naturally emitted isoprene and terpenes. The various source estimates of the hydrocarbons will be briefly discussed below.

Automobile exhaust

The most important anthropogenic source of light NMHC are the emissions from automobiles. Most of these emissions result from the incomplete combustion in gasoline engines. To estimate the strength of this source we have to know the global consumption of gasoline by cars and the globally averaged emission factor for NMHC. Both numbers are available from the literature. They are however not up to date.

For the global gasoline consumption we used the estimate for the year 1976 by Logan et al. (1981) which amounts to 620×10^{12} g gasoline/yr. The emission factor was derived from the estimates of NMHC emissions from gasoline powered cars and the gasoline consumption in West Germany for 1978 (Luftreinhaltung '81). It corresponds to 2.6 % by weight. This value is close to emission factors quoted for American cars (NAS, 1976). It does not take into account any re-

duction of NMHC emission due to the installation of catalytic converters.

The product of these two numbers gives the total NMHC emission of 16×10^{12} g/yr shown in the second column of Table 1.

To assign individual emission rates to the various NMHC, the average composition of the exhaust has to be known. The composition is variable depending on the type of gasoline utilized and the operating conditions of the engine. We used the exhaust composition measurements given by Nelson et al. (1982) for Sidney. They agree reasonably well with the exhaust composition from US studies (cf. NAS, 1976).

As Table II shows, C_2H_4 , C_2H_2 , C_3H_6 , C_4H_{10} , and n-, i- C_5H_{12} are among the dominant species. The aromatic hydrocarbons, benzene, toluene, and the xylenes, are also abundant. The lighter hydrocarbons are generated in the combustion process, unburned fuel is responsible for the hydrocarbons with carbon numbers $C \geq 4$.

The emission factor for Diesel engines is lower, only about a factor 0.5 of that of gasoline engines. In addition the global use of Diesel fuel was only 158×10^{12} g/yr in 1976 (Logan et al., 1981). Thus the total NMHC emission from Diesel exhaust is only 3×10^{12} g/yr. The composition of Diesel exhaust is different from that of gasoline exhaust especially for carbon numbers $C > 5$.

Evaporation of fuel from automobiles

Evaporation of fuel in automobiles is another source of NMHC. It occurs in two ways: a) The so-called heat-soak loss from carburetors. This term describes the evaporation from the carburetor as it heats up after engine shutoff. Since the evaporation is essentially complete the resulting emissions have the composition of the fuel itself. b) Losses from fuel tanks. Since that loss is via the vapor phase, the emissions depend also on the vapor pressure

of the individual fuel components, i.e. the light, low boiling NMHC escape preferentially. The total evaporative loss is estimated to be about 25 % of the exhaust emissions (Stern, 1968; NAS, 1976; Nelson et al., 1982). It consists mostly of the butanes and i-pentane (NAS, 1976; Nelson et al., 1982).

Evaporation losses from distribution and refineries

Emissions also occur during distribution and refining of fuels. The emission factors quoted in the literature vary considerably (Robinson and Robbins, 1969; Stern, 1968). Here we use a total NMHC emission factor of 0.5 % weight NMHC per weight fuel for distribution and 0.1 % for refining, which seem to apply for West Germany (Luftreinhaltung '81). Assuming the same composition as for the evaporation losses from cars, we obtain the numbers shown in Table 1.

Losses of natural gas

Besides CH_4 , natural gas also contains higher alkanes notably C_2H_6 , C_3H_8 , iC_4H_{10} , nC_4H_{10} . Thus losses and seepage of natural gas lead to emissions of NMHC. They are more difficult to estimate. Firstly the composition of natural gas varies widely. Dry natural gas, i.e. natural gas resulting from biogenic decomposition of organic matter contains only traces of NMHC, whereas natural gas associated with crude oil deposits, so-called wet natural gas can have substantial amounts of NMHC, and so has gas from coal deposits. In the following we assume an average methane to NMHC ratio of $\text{CH}_4/\text{NMHC} = 5$ as it is found for the average natural gas in the US.

Little is also known about the average loss rate of natural gas. CH_4 budgets have assumed factors of 1 - 5 %. We will assume that 3 % of the total natural gas production gets lost to the atmosphere. The resulting emissions of C_2H_6 , C_3H_8 and C_4H_{10} are shown in Table 1.

Chemical industry, solvents

Somewhat smaller losses occur in the chemical industry, and mostly in form of compounds not of interest here. The emissions in form of solvents on the other hand is quite large. But again most of the solvents (used in paints, dry cleaning etc.) are halogenated compounds, alcohols or esthers of lesser interest here and are not detailed in Table 1.

Combustion of oil and coal

Combustion of oil and coal also releases NMHC at an emission rate shown in table II. Since the hydrocarbon emissions are relatively low and their composition poorly known, no detailed estimates are given in Table 1.

Biomass burning

Under this heading we include the emissions by slash and burn agriculture, deforestation, burning of savanna and bushland, forest wild fires, burning of fuel wood, burning of agricultural wastes, and burning of industrial wood. These add up to the burning of 6800×10^{12} g/yr of biomass (Crutzen et al., 1981). There are various estimates for the emission factors (Robinson and Robbins, 1968; Duce et al., 1982; NAS, 1976). We assume a relatively low average emission factor of 0.2 % weight NMHC per weight fuel. For the composition we used the relative values given by Stephens and Burleson (1969). Since this is such a mixture of sources with different emission factors and composition, the estimates given in Table 1 are very tentative and uncertain. They also involve large extrapolations of local measurements to global areas. But they indicate that despite the low emission factor biomass burning is potentially a big source and merits further investigation.

Foliage

The emissions of hydrocarbons by foliage are apparently enormous (Zimmerman et al., 1981). But the gases emitted, isoprene and terpenes do not fit into NMHC discussed here. Moreover they are very shortlived and measurable concentrations exist only in the immediate environment of the sources. Their immediate impact on atmospheric chemistry is local or regional and there it may be overwhelming. Their global impact proceeds through the products formed during their oxidation, CH_2O , H_2 , CO , and possibly O_3 . They will not be discussed further. However, leaves, especially when damaged also emit minor amounts of C_2H_6 and C_2H_4 . An estimate for these emissions is included.

Microbial production of NMHC

Most of the CH_4 found in the atmosphere has been released after microbial production in anoxic environments (Ehhalt, 1974). This emission rate totals about 500×10^{12} g CH_4 /yr. Under the same conditions NMHC may also be produced and released. Van Cleemput et al. (1981) report the production of CH_4 , C_2H_4 , C_2H_6 , C_3H_8 after incubation of soil samples. The NMHC production is however small. Relative to CH_4 the production of C_2H_4 was on the order of 5×10^{-3} , that of C_2H_6 was 7×10^{-4} , and that of C_3H_8 was 4×10^{-4} on a volume to volume basis. Extrapolated to the globe with the help of above CH_4 emission one would obtain 4.4×10^{12} g C_2H_2 /yr, 0.7×10^{12} g C_2H_2 /yr, and 0.5×10^{12} g C_3H_8 /yr. These estimates are entered also into Table 1.

Oceans

Another important source of NMHC is the ocean. Light NMHC (C_2H_6 , C_2H_4 , C_3H_8 , C_3H_6) are dissolved in surface ocean water at large supersaturations with respect to their atmospheric concentrations (Lamontagne et al., 1974; Swinner-

ton and Lamontagne, 1977). Thus they effuse into the atmosphere. For certain ocean areas the fluxes can be estimated (Rudolph and Ehrlert, 1981). At 70° N latitude they amount to a few mg/m²/yr. Extrapolated to the globe we obtain the numbers shown in Table 1.

There are indications, however, that surface waters of the tropical oceans are by a factor 3 more supersaturated in C₂H₄ and C₃H₆ (Lamontagne et al., 1974). This means that the tropical ocean could be a stronger source for C₂H₄ and C₃H₆ (but not for C₂H₆ and C₃H₈) than estimated from the data from 70° N. With the atmospheric mixing ratios of C₂H₄ and C₃H₆ given in the previous chapter, and the estimated lifetimes of 0.7 days for C₂H₄ and 0.3 days for C₃H₆ in the tropics, we can also calculate the sink strength over the tropical ocean between 10° N to 10° S, assuming a well mixed boundary layer of 1 km depth. The resulting values are 5 x 10¹² g C₂H₄/yr and 10 x 10¹² g C₃H₆/yr. These values are entered separately in Table 1. As in most of the previous estimates the extrapolations involved in the estimate of the oceanic source strengths are enormous. The uncertainties are large. Nevertheless the estimates indicate that the oceans may be a large source of NMHC and merit further investigation.

This concludes the list of NMHC sources known to us. There might be others which have not been identified yet, and the ones presented, especially the natural sources have very large uncertainties. It should be reemphasized that the present exercise was a first attempt at a budget of the NMHC and that the estimates presented, sometimes nothing more than guesses, are preliminary meant more as guidelines for future research than as final answers.

Table 1a: Global estimates of anthropogenic hydrocarbon emissions into the atmosphere (10^{12} g/yr)

Source	CH ₄	NMHC	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	n-C ₄ H ₁₀	n-C ₅ H ₁₂	i-C ₅ H ₁₂	Benzene	Toluene	p, m, o-Xylene	Isoprene	Terpenes
1. Automobile exhaust a. gasoline engines b. diesel engines	.9	16 3	.2	1.9	1.4	.02	.8	.4	.5	.8	.8	1.7	1.5		
2. Evaporation losses from cars	-	4	-	-	-	-	-	.4	.4	.7	.06	.3	.2		
3. Evaporation losses during distribution and refining	-	6	-	-	-	-	-	.6	.5	1.0	.08	.4	.3		
4. Natural gas losses	25	5	1	-	-	1	-	1*							
5. Coal burning	-	3	-												
6. Oil burning	-	1	-												
7. Chemical industry	-	3	.1	.3							.1	.1			
8. Solvents	-	15	-									1	.5		

*including i-C₄H₁₀

Table 1b: Global Estimates of natural hydrocarbon emission into the atmosphere (10^{12} g/yr)

Source	CH ₄	NMHC	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	n-C ₄ H ₁₀	n-C ₅ H ₁₂	i-C ₅ H ₁₂	Benzene	Toluene	p, m, o-Xylene	Isoprene	Terpenes
9. Biomass burning	60	14	4.1	4	.6	1.7	3.8								
10. Foliage		(1.5)	.5	1										350	480
11. Microbial Production	500	5.7	.7	4.4			.6								
12. Oceans tropical rest	5	15 6	1	5 2		1.3	10 1.6								

Disregarding isoprene and terpenes the organic emission from natural and anthropogenic sources appear approximately the same. They total about 100×10^{12} g/yr, or about 20 % of the global CH_4 emission rate. However, only 11×10^{12} g/yr of the anthropogenic emissions are in the C_2 to C_5 range, whereas all of the natural emission, 42×10^{12} g/yr, fall, in that category. They combine to 50×10^{12} g/yr or 10 % of the CH_4 emissions. Based on this balance the global impact of C_2 - C_5 hydrocarbons on the tropospheric chemistry would be on the order of 10 % of that of CH_4 . However much of these emissions take place in the midlatitudes of the northern hemisphere. The photochemistry in the boundary layer of a large part of that region may indeed be dominated by NMHC rather than by CH_4 , and as pointed out above most of the experiments on tropospheric chemistry have been and are carried there, a point which must be kept in mind when interpreting these data.

Conclusion

Our knowledge about the atmospheric chemistry and budget of hydrocarbons is still extremely patchy. It resembles a puzzle where many of the pieces are missing. This makes it difficult to present a systematic picture. At the same time there is sufficient information to establish that NMHC are certainly of high regional importance and very probably of global importance. In both environments multiphase chemistry of organic molecules seems to play an important role. The many gaps in our knowledge of the chemistry and budget of organic compounds in the atmosphere present a challenge. A challenge that we can begin to meet, since with the advance of the various highly sensitive chromatographic techniques and others like the Lamma Sonde the tools for this trade have become available.

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