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Summary

While methane is chemically quite inert to reactions with atmospheric molecular species, it does react with atomic species and molecular radicals. Because of its relatively large abundance in the global troposphere and because of the apparent annual increase of its concentration, it is worthwhile exploring the role of methane in tropospheric chemistry, especially the role in air pollution.

From a detailed analysis of the reactions of methane with atmospheric species we conclude that while methane does play a role in generating the general background of ozone that permeates the global troposphere, it plays only a minor role in urban and rural ozone formation. In urban areas, most of which fail to meet the ozone standards established by the Clean Air Act, the prime facilitators of ozone formation are various higher hydrocarbon emissions. In rural and forested areas, biogenic emissions of terpenes, pinenes and isoprenes take a dominant role in creating ozone via their peroxy radical. Thus, the omission of methane in urban and rural ozone modeling is justified. The models should use a general ozone background level which in most areas of the U.S. amounts to 10-30 ppb. This background ozone may be due in part to global methane concentrations. Further, for ozone control purposes in exceedance areas, little would be gained by monitoring methane at the emission sources or in the ambient.

Annually between 400-800 million tons (MTy^{-1}) of CH_4 are emitted, of which 100-200 MTy^{-1} come from enteric fermentation, 280-500 MTy^{-1} from wetlands and rice paddies, 16-50 MTy^{-1} from fossil fuel leakage and combustion and the rest from other minor sources. These emissions produce in the northern hemisphere an annual average concentration of methane in air of about 1600-1700 parts per

billion by volume, abbreviated henceforth ppb. The concentration appears to increase by about $1\% \text{ y}^{-1}$. For comparison, the tropospheric abundance of other hydrocarbons ranges from 0.1-10 ppb. In urban, polluted areas both methane and non-methane-hydrocarbon (NMHC) concentrations could be larger. Unfortunately, few measurements are available that include the whole spectrum of hydrocarbons.

The most important tropospheric reaction of methane is with the hydroxyl radical OH. This reaction initiates a chain that leads to the formation of the methyl peroxy radical CH_3O_2 , and to a lesser extent to formaldehyde HCHO and methyl nitrate CH_3ONO_2 . The CH_3O_2 radical may be an important oxidant that converts atmospheric nitric oxide NO into nitrogen dioxide NO_2 . Nitrogen dioxide is the major precursor of ozone O_3 . However, peroxy radical formation is much more rapid from higher alkanes, unsaturated hydrocarbons and aromatic hydrocarbons. The NMHC's react 25-830 times faster with hydroxyl than methane. The extent to which CH_4 contributes to O_3 concentrations is very much dependent on the ratio of ambient concentrations of NMHC/ CH_4 . In our estimation, methane is a contributor to the general tropospheric ozone concentration or "background" ozone, which amounts to 10-30 ppb in the US. In rural and forested areas, where biogenic emissions of terpenes, pinenes and isoprenes are large, these hydrocarbons form rapidly peroxy radicals contributing to excess ozone formation over that of the general background. In urban areas, there are large emissions of higher hydrocarbons due to evaporation of fuels, solvents and paints, industrial (e.g. refinery) emissions, and incomplete combustion of fuels. In urban areas, we expect that these emissions are the prime facilitators of ozone formation, as well as the precursors of other "smog" ingredients, e.g. aldehydes, ketones, acids, organic nitrates and peroxyacetyl nitrate (PAN).

1. Introduction

Methane is chemically quite inert. Nevertheless, because of its large abundance in the lower layers of the atmosphere, and because of the expectation that this abundance will further rise as a consequence of population and economic growth, it is worthwhile exploring just how inert is methane, or conversely, what is the role of methane in tropospheric chemistry in general, and in air pollution in particular. In air pollution modeling, it is customary not to include methane emissions or ambient levels of methane as a factor in estimating the levels of air pollutants that will accrue due to the emissions. Emission inventories of reactive hydrocarbons are usually given in terms of non-methane-hydrocarbons, NMHC, with the assumption that methane emissions do not play a significant role in atmospheric chemistry. How justified is this assumption is the subject of the following discourse. We note that here only the role of methane in tropospheric chemistry is explored; the role of methane as a "greenhouse" gas will be the subject of a follow-on paper.

2. Methane: Physico-chemical Properties

The methane molecule, CH_4 , is chemically stable as all the outer shell electrons of the carbon atom are paired with the single electrons of the four hydrogen atoms. Therefore, methane has a low reactivity to other molecules. Methane has virtually no dipole moment (polarity), therefore, it is not readily absorbed or dissolved in polar solvents such as water. The absence of electropolarity also causes the methane molecule to exist in the gaseous, non-condensed form to very low temperatures. Its boiling point is -164°C , and its freezing (melting) point is -182°C .

These properties explain the fact that CH_4 is a relatively stable species in the atmosphere with an estimated life time of about 8 years (Khalil and Rasmussen, 1983). Part of the atmospheric CH_4 is lost due to adsorption on soil and vegetation, part to upward diffusion into the stratosphere, the rest is lost due to some chemical reactions in the atmosphere, notably with atomic species, such as H, N, O and Cl and with radicals, such as OH, HO_2 and organic radicals usually denoted as $\text{R}\cdot$.

It is due to the reactions with atomic species and radicals that CH_4 does not persist even longer in the atmosphere and that it burns rather rapidly (almost explosively) when mixed with the right proportion of air and ignited

with an electric spark or a torch. The spark or the torch provide the first atoms and radicals that start the chain reaction of the CH_4/O_2 conflagration.

It is the individual reactions of CH_4 with some atmospheric species that we wish to explore further, in particular, those that lead to the formation of air pollutants, such as ozone (O_3), aldehydes, peroxy compounds, and organic nitrates.

3. Methane: Sources and Concentrations

Before dwelling on the chemistry of methane, let us review the sources that contribute to the atmospheric burden of CH_4 , and the trend of this burden over recent times. Natural sources for atmospheric CH_4 are wetlands, termites, wild fires, and enteric fermentation of wild ruminants. Enteric fermentation of domesticated ruminants are considered anthropogenic sources. Also, rice paddy emissions, a kind of wetland, are considered to be anthropogenic. Other anthropogenic sources are coal mine venting, associated gas from oil wells, leaks from natural gas wells, storage, pipelines and end use. Natural gas typically contains 90% methane, 5% higher alkanes and 5% other gases.

The estimates of the emission rates from both natural and anthropogenic sources are highly uncertain. Table 1 gives estimates of emissions by source categories performed by two groups of authors. Apparently, there is a wide range of estimates for each source category, as well as for the total. The sum total of emissions ranges from about 550 to 825 million tons per year. The fossil fuel category accounts for $16\text{--}50 \text{ MTy}^{-1}$, that is 2–12.5% of the total.

Ambient concentrations of CH_4 vary both in space and time. Figure 1 presents the current latitudinal distribution of annual mean CH_4 concentrations at 19 monitoring sites. These sites are located away from potential local emission sources of CH_4 , such that their measurements represent the average "background" concentration as a function of latitude. In the northern hemisphere the annual mean concentration ranges from 1600–1700 ppb.

A long term record of ambient CH_4 concentrations is not available. Figure 2 presents the measurements at Cape Meares, OR from late 1979 into 1984. Over this period the ambient concentration increased from 1620 ppb to 1690 ppb, that is by about $1\% \text{ y}^{-1}$. It appears that CH_4 concentrations are on the increase as is everything else that is related to human activities.

Table 1. Methane Emissions (million tons per year)
 Column I, Ehhalt and Schmidt (1978);
 Column II, Khalil and Rasmussen (1983)

<u>Category</u>	<u>I</u>	<u>II</u>
Enteric fermentation	100-200	120
Rice paddies	~ 280	95
Wetlands	90-300	150
Biomass burning	--	25
Fresh water lakes	1-25	10
Oceans	1-17	13
Tundra	0.3-3	12
Fossil fuel	16-50	40
Other	--	90
Total	586-825	555

4. The Chemistry of Photo-oxidants

Before exploring the role of methane in tropospheric chemistry, and in particular its role in photo-oxidant chemistry, let us review the most salient features of that chemistry. The term photo-oxidants is commonly used to describe a mixture of gaseous and particulate matter, including nitric oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), hydrocarbons (HC), ozone (O_3), aldehydes (RCHO), ketones (R_2CO), inorganic nitrates (e.g. nitric acid, HNO_3 , and ammonium nitrate, NH_4NO_3), organic nitrates (RNO_2), organic radicals ($\text{R}\cdot$)*, peroxy radicals ($\text{RO}_2\cdot$) peroxyacetyl nitrate ($\text{CH}_3\text{OCOONO}_2$, PAN), and various inorganic and organic particles. While most, if not all, of the above compounds can be harmful to human health, animals and plants, only a few representative photo-oxidants are regularly measured. Ambient standards (i.e. maximum concentration levels) are set only for three ingredients of photo-oxidants, O_3 , NO_x and HC. In part, this limitation stems from the difficulty and expense of measuring all the photo-oxidants, and in part, because the ambient concentrations of most photo-oxidants are proportional to the measured ones.

* The dot denotes an unpaired electron which is the attribute of a radical. In subsequent text the dot will be omitted.

In fact, the single most significant measure of photo-oxidants is the ambient concentration of ozone, O_3 . Generally, the measured ambient concentration of ozone is indicative of the "air quality." The national ambient air quality standard (NAAQS) for ozone is 120 parts per billion by volume (ppb) (235 micrograms per cubic meter), 1-hourly average concentration, which is not to be exceeded more than once in a year. This standard was established after clinical studies showed that inhaling air that contains larger concentration of ozone than 120 ppb for longer than one hour caused many individuals to suffer respiratory dysfunctions. It is also known that high concentrations of photo-oxidants in the air cause pathological changes in plants and decreased growth rate, including significant crop losses.

Although the NAAQS for ozone is set at 120 ppb, practically every metropolitan area in the US exceeds that standard many more times than once in a year. In 1984, Los Angeles exceeded the standard 130 days, Houston 30, St. Louis 15, Chicago 10, New York 30, and Washington 5 days. For this reason great effort (and expense) is being spent to bring these communities into compliance with NAAQS. In order to gain perspective over the proposed and promulgated regulatory measures we must understand the chemistry of formation of photo-oxidants in general, and ozone in particular.

The most important step in ozone formation is the photo-dissociation of nitrogen dioxide, NO_2 :



Here $h\nu$ designates a photon, a quantum of energy from the solar spectrum, and O is atomic oxygen. The minimum required energy of this photo-dissociation corresponds to a wavelength of 4200 Angstrom units, which places it in the blue end of the visible solar spectrum. Nitrogen dioxide is one of the few gaseous molecules that can dissociate in visible light. The above photo-dissociation is followed by the following reaction:



Here M designates a third molecule. The recombination of atomic oxygen with molecular oxygen can only proceed with the intermediation of a third molecule that carries away the excess kinetic energy of the collision. However, at

normal atmospheric pressure there is an abundance of both molecular oxygen and third molecules (e.g. nitrogen) such that reaction (2) proceeds quickly.

If reactions (1) and (2) were the only instruments of forming ozone, the concentration of the latter could not exceed the concentration of NO_2 , provided no fresh NO_2 is supplied to the volume of air in which reactions (1) and (2) take place. However, nitric oxide, NO , formed in the photo-dissociation (1) recombines with ozone

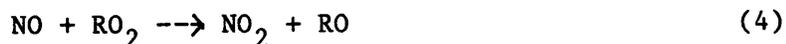


In full sunlight, all these reactions proceed fast, and a so-called "photo-stationary state" is established in which the ozone concentration is given by

$$[\text{O}_3] = \frac{k_1[\text{NO}_2]}{k_3[\text{NO}]}$$

where square brackets designate concentrations, and the k 's are the rate constants for the numbered reactions. Typically, the ratio $k_1/k_3 = 20$ ppb and $[\text{NO}_2]/[\text{NO}] < 1$. Thus, if only NO_x pollutants were present, the O_3 concentration could not exceed 20 ppb, which is contrary to observations.

In studies conducted over the past several decades, both in the ambient and in the laboratory ("smog chambers"), it was found that many more reactions participate in the formation of ozone, of which the most significant is



where RO_2 is a peroxy radical that readily oxidizes nitric oxide into nitrogen dioxide. In this fashion, the NO formed in the photo-dissociation (1) is very rapidly recycled into NO_2 , the latter molecule becoming again available for photo-dissociation.

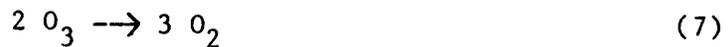
The all important oxidant RO_2 (R = organic radical) is formed in complex photo-chemical processes (see below) involving mainly the presence in the air of hydrocarbons (HC). The sources of hydrocarbons are in part anthropogenic, such as incomplete combustion of fuels, evaporation of fuels and solvents, and in part biogenic, such as the evaporation of organic matter from leaves, pines and decomposition of plants and trees.

With the inclusion of the oxidants RO_2 and their precursors in the rate equations, the estimation of ambient ozone concentration becomes quite complicated. As a minimum, the following generalized reactions must be included:



where RH is a hydrocarbon, OH is the hydroxyl radical (present in the atmosphere from the photo-dissociation of hydrogen peroxide, H_2O_2 , or from the reaction of water vapor with an excited form of atomic oxygen).

Another reaction needs to be included, and that is the destruction of ozone:



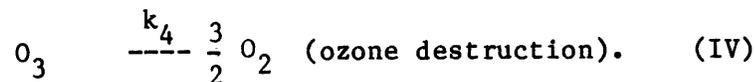
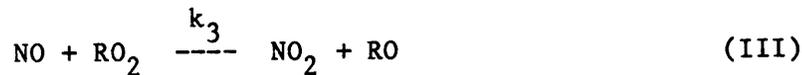
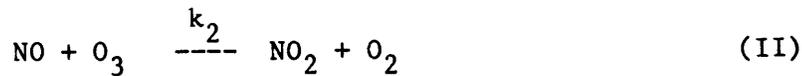
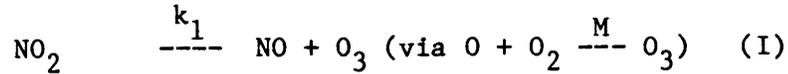
Ozone, being highly reactive, interacts with numerous natural and artificial ingredients of the polluted atmosphere. It also adsorbs onto surfaces (causing the destruction of rubber, for example, as well as damage to leaves and other living tissues).

The estimation of ambient ozone concentrations requires the simultaneous solution of the rate equations (1) - (7) with specification of all rate coefficients and initial concentrations of the precursors. Numerous "models" exist for the estimation of ambient ozone concentrations that may result from the above generalized chemical reaction sequence (see, e.g. the review of Seinfeld, 1988). Some models include tens, and even hundreds of chemical reactions. Others require only the specification of the precursor concentrations, such as NO_x , the ratio NO/NO_2 , the non-methane-hydrocarbon (NMHC) concentration, and the "reactivity" distribution of the NMHC. Most models require also the specification of local climatological information, such as solar intensity, winds, and the mixing height. (The latter is the height up to the first temperature inversion. It is assumed that the atmosphere is well mixed, i.e. isotropic, up to that height.)

For the understanding of the role of methane in ozone formation we use a highly simplified chemical model. We believe this model contains the most

salient features of the chemical mechanisms operative in a polluted atmosphere. In this model no climatological input is necessary. The purpose here is not to propose the simpler model in lieu of more complex ones, but rather to show in particular the effect of the hydrocarbon reactivity upon ozone formation.

The following generalized chemical reaction sequence is used:



We make the further simplifying assumptions:

1. The concentration of $[\text{NO}_x] = [\text{NO}_2] + [\text{NO}]$ is constant, and is an independent variable of the model. At the beginning of the diurnal cycle (before sunrise) $[\text{NO}_2]_0 \equiv [\text{NO}_x]$, i.e. there is no NO present.
2. Ozone formation is instantaneous upon the photodissociation reaction (I).
3. The peroxy radical concentration is constant. Actually, the model uses a constant value of the product $k_3 * [\text{RO}_2]$. This product is an independent variable of the model. This is the most drastic simplification of the model; it is a surrogate of tens of chemical reactions used in more complicated models. However, as will be seen, this simplification allows us to derive important conclusions on maximum ozone concentration formed as a function of the precursor hydrocarbon concentration and its reactivity.
4. The photodissociation rate constant k_1 is assumed to vary over the daylight hours in a form $k_1 = k'_1 \sin \omega t$, where k'_1 is the photodissociation rate at solar noon, and ω is the solar zenith angle.
5. The ozone destruction rate constant k_4 , which lumps together chemical destruction and dry deposition, is a dependent variable of the model. The model program specifies that k_4 takes the magnitude such that upon the completion of a diurnal cycle (before sunrise) the ozone concentration returns to the beginning value.

6. The beginning value of ozone concentration is an independent variable of the model; it is the general "background" concentration of ozone. In most of the US, the background concentration varies between 10-30 ppb.

The results of the model calculations are presented in Figure 3. The independent variables are specified in the figure caption. The shape of the diurnal variation of ozone concentrations obtained from this simple model is remarkably similar to the actual observed shape in many urban and rural areas in the US, and also to the output of the more complex models.

Three curves are presented in Fig. 3. For each curve, the initial conditions are the same, viz. $[\text{NO}_2]_0 = [\text{NO}_x] = 10$ ppb, $[\text{O}_3]_0 = [\text{O}_3]_{\text{bkg}} = 30$ ppb. The three curves are obtained by varying the magnitude of the product $k_3 * [\text{RO}_2]$ from 0.002 to 0.02 to 0.2 s^{-1} . The corresponding peak ozone concentrations, achieved at about 11 hours after sunrise, are 45, 90, 140 ppb. Subtracting the background value of 30 ppb, the net peak production of ozone is 15, 60, 110 ppb. Since $[\text{NO}_x] = 10$ ppb, 1.5, 6, 11 times as high concentrations of ozone are produced as is the NO_x concentration, depending on the value of $k_3 * [\text{RO}_2]$.

Let us analyze the meaning of the dependence of ozone formation on $k_3 * [\text{RO}_2]$. Once a peroxy radical RO_2 is present, it probably oxidizes NO to NO_2 at the same rate k_3 regardless of the nature of RO_2 . Thus, most likely it is the concentration of RO_2 that determines the ozone production efficiency, not the oxidation rate constant k_3 . Now, the key reactions in producing RO_2 are (see p. 7)

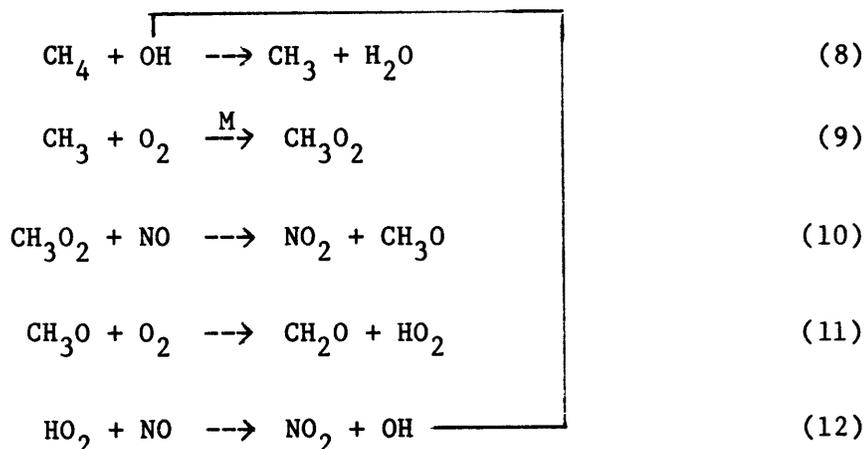


In effect, it is the reactivity of RH (the "hydrocarbon") toward the hydroxyl OH that determines the net production of ozone from a given concentration of NO_x . This is the crucial conclusion not only from this simple model, but of most photo-oxidant models, regardless of their complexity (see, e.g. Seinfeld, 1988). Basically, this conclusion also leads to the regulatory requirements by federal and state authorities to reduce both NO_x and NMHC emissions in order to reduce peak ozone concentrations. In fact, some models, notably the Empirical Kinetics Modeling Approach (EKMA), used widely in designing control

strategies, indicate that over a large range of NO_x/NMHC ratios it is more effective to reduce NMHC concentrations than it is NO_x concentrations in order to reduce ozone concentrations. At this point we do not wish to argue the relative merits of NO_x vs. NMHC reductions; however, our model strongly supports the notion that it is the ambient concentration of the oxidants RO_2 that determines the peak concentration of O_3 from a given concentration of NO_x . In the following section we shall examine if methane contributes significantly to the formation of RO_2 , and hence to ozone formation.

5. Methane's Role in Photo-oxidants

In analogy to the customary hydrocarbon photo-oxidation reaction mechanism (see e.g. Seinfeld, 1986), we may write the following sequence for methane



According to this sequence, the hydroxyl radical reacts with methane to form the methyl radical CH_3 . This in turn forms the methyl peroxy radical CH_3O_2 which serves as the oxidant for the NO to NO_2 recycling. Furthermore, a hydrogen peroxy radical is formed (reaction 11), which also can oxidize NO to NO_2 (reaction 12). A hydroxyl radical is regained which restarts reaction (8). Thus, the reaction sequence (8)-(12) could be self-perpetuating, although the cycle is expected to be slow.

Several laboratory measurements have been reported on the rate of the reaction between light hydrocarbons and hydroxyl. The measured rates are listed in Table 2 (NBS, 1977).

Table 2. Rate of hydrocarbon reaction with hydroxyl

Hydrocarbon	Rate ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)*	$k_{\text{NMHC}}/k_{\text{CH}_4}$
CH ₄ methane	(8.3 ± 1) exp-15	1
C ₂ H ₆ ethane	(2 ± 1) exp-13	25
C ₃ H ₈ propane	(2 ± 1) exp-12	250
C ₄ H ₁₀ butane	(2.5 ± .5) exp-12	330
C ₂ H ₄ ethene	(5 ± 2.5) exp-12	625
C ₂ H ₂ acetylene	(2 ± 1) exp-13	25
C ₆ H ₆ benzene	(1 ± .2) exp-12	830

*Average of listed measurements at T = 300°K.

Methane reacts with hydroxyl 25-830 times slower than the higher alkanes, unsaturated hydrocarbons and aromatic hydrocarbons. However, it is the relative abundance of the hydrocarbons that needs to be considered in the production of ozone. In Section 3 we have seen that the global tropospheric abundance of CH₄ is in the order of 1500-1700 ppb. The measured global tropospheric abundances of light hydrocarbons (e.g. C₂H₆, C₃H₈, C₂H₄, C₂H₂, etc.) are in the order of 0.1-10 ppb (World Meteorological Organization, 1985). Comparing the abundances and the rate of reactions we conclude that methane does contribute to the global tropospheric level of ozone. Probably, the general "background" level of ozone is in part due to methane. In rural areas, especially in coniferous forests, the emission level of some hydrocarbons is large, such as terpenes, pinenes and isoprenes. In those areas we expect that primarily these hydrocarbons form peroxy radicals and consequently contribute to the higher levels of ozone. In a rural area of Pennsylvania, Trainer et al. (1987) attributed the following increments to peak ozone concentrations of 120 ppb: background 20 ppb, methane and carbon monoxide 35 ppb, biogenic isoprene 50 ppb, anthropogenic NMHC 15 ppb.

In urban areas, there are large emissions of hydrocarbons from industrial and transportation sources, such as evaporation of solvents, paints and fuels, and incomplete combustion products of fuels. Here, the ratio of methane to non-methane hydrocarbons is much smaller than the global tropospheric average.

In urban areas most likely the anthropogenic NMHC take the dominant role in producing peak ozone concentrations. In Table 3 a partial listing is given of

the most abundant hydrocarbons in Los Angeles. Since methane measurements were not reported, we inserted an average tropospheric abundance of 1600 ppb. In column 3 the concentration ratio $[\text{NMHC}]/[\text{CH}_4]$ is given. Multiplying this ratio with the ratio of rate constants (Table 2, column 3), we expect that in the Los Angeles area methane competes successfully for OH radicals only with ethane and acetylene. The other hydrocarbons, notably ethene, will react much faster with hydroxyl than methane.

Hough and Derwent (1987) modeled the ozone concentration in the London airshed by using a complex chemical reaction set and assumed initial concentrations of the precursors, including methane (the assumed concentration happened to be 1600 ppb). According to their modeling results, methane contributes only between 4-7.5% of the ozone concentration in London.

While detailed monitoring of hydrocarbon species, including methane, in urban areas in the US is scarce, we do not expect that the relative abundance of methane to other hydrocarbons would be such that methane plays a significant role in ozone production in urban areas above the general background level.

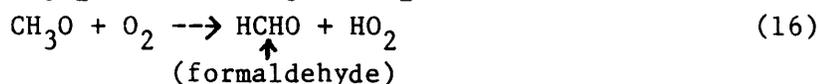
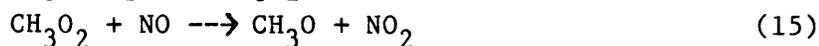
Table 3. Hydrocarbon concentrations in the Los Angeles area.
Partial listing from EPA (1987)

<u>Hydrocarbon</u>	<u>Concentration (ppb)</u>	<u>$[\text{NMHC}]/[\text{CH}_4]$</u>
Methane	1600*	1
Ethene	943	0.6
Ethane	49	0.03
Butane	49	0.03
Acetylene	38	0.02
Propane	37	0.02
Toluene	20	0.01
Xylene	20	0.01
Pentane	16	0.01
Hexane	10	0.006
Cyclohexane	10	0.006
Benzene	8	0

*assumed, not measured

6. Further Tropospheric Reactions of Methane

There may be a potential alternative reaction sequence with OH that leads to formaldehyde production, a toxic chemical:



Since reaction (13) has been shown to be slow, and NO concentrations are limited even in highly polluted areas, it is not expected that significant concentrations of formaldehyde will ensue from this sequence. A much stronger source of formaldehyde appear to be automobile emissions, in particular from oxygenated fuels, such as methanol and ethanol (Alson and Baines, 1982), as well as from more reactive hydrocarbons in a similar sequence as (13-16) above.

An alternative reaction to (15) is



Reaction (15a) yields methyl nitrate, which is a strong respiratory and eye irritant. Again, because of the slowness of (13), no significant quantities of methyl nitrate will be formed by this route.

Atomic oxygen will react with methane



This reaction could be a source of hydroxyl that starts the ozone production sequence of hydrocarbons, as well as the methyl radical CH_3 , which recombines with O_2 to form the peroxy radical CH_3O_2 (reaction 14). However, reaction (17) is expected to be rare, (a) because the concentration of atomic oxygen in the troposphere is small, and if present, atomic oxygen will recombine with O_2 , a much more abundant species than methane.

Similarly atomic chlorine will react with methane



forming the methyl radical and hydrochloric acid. In fact, methane can react with molecular chlorine Cl_2 in the presence of sunlight. In sunlight, Cl_2 photodissociates into atoms, thereby initiating reaction (18).

7. Conclusions

Methane at ambient temperatures is quite inert to normal atmospheric constituents such as O_2 . However, in the presence of "energetic" constituents such as radicals and atomic species, methane will enter into chemical reactions. One such species is hydroxyl OH, which initiates a chain sequence leading to the formation of the methyl peroxy radical CH_3O_2 . The peroxy radical is an important oxidant that converts nitric oxide NO to nitrogen dioxide NO_2 . The latter, in turn, photodissociates, generating ozone O_3 . In remote areas of the world, where methane is much more abundant than other hydrocarbon species, the methyl peroxy radical may be the principal recycler of NO to NO_2 , and hence an important contributor to global tropospheric ozone concentrations. In rural areas, biogenic hydrocarbons will take precedent over methane in forming ozone. In urban areas, anthropogenic emissions of higher alkanes, unsaturated hydrocarbons and aromatic compounds will dominate the ozone production process.

We conclude that the omission of methane in urban air pollution monitoring and modeling is justified; however, methane may play a significant role in the generation of the global tropospheric ozone content.

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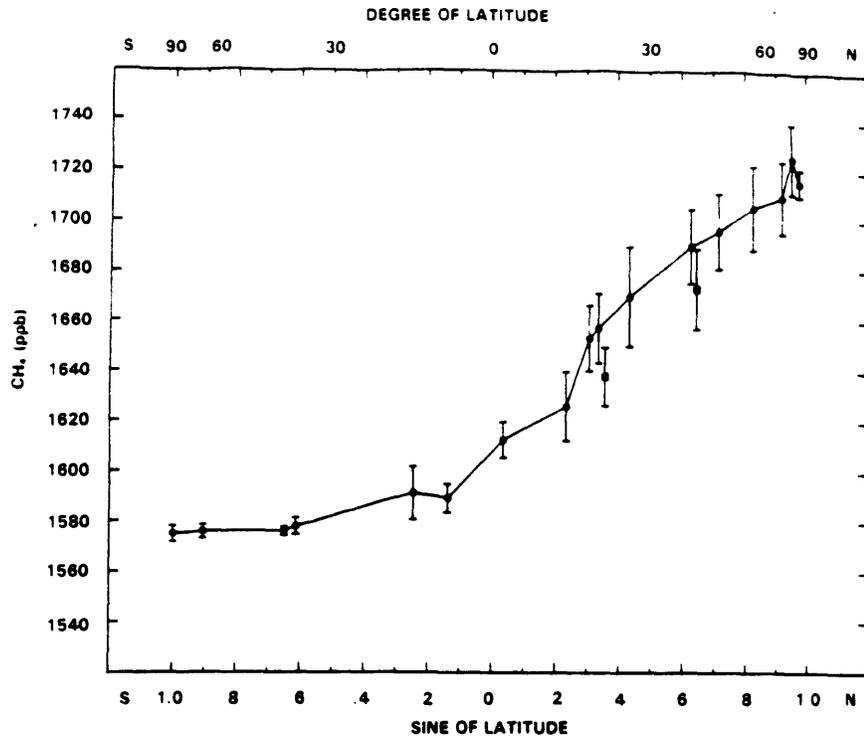


Fig. 1 Latitudinal distribution of annual mean CH_4 concentrations in ppb at 19 sampling sites (Steele et al., 1987)

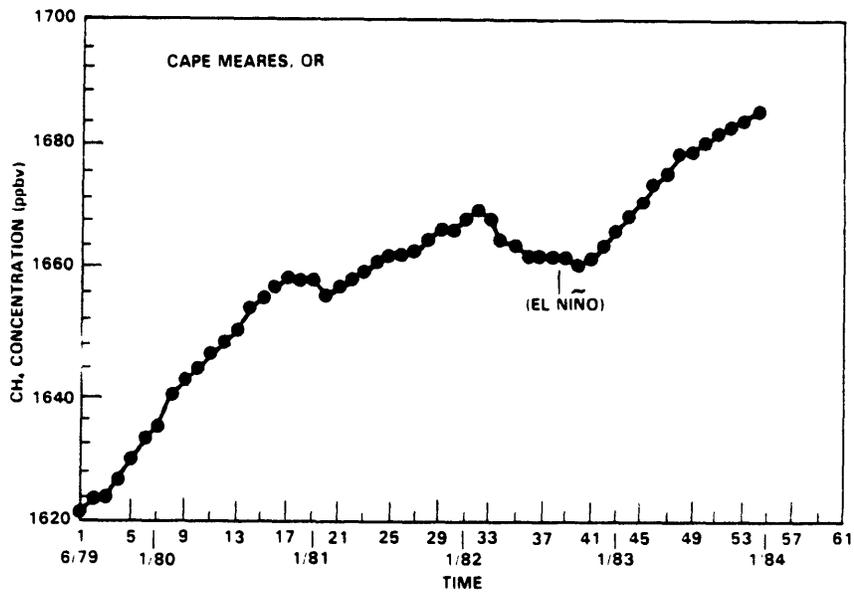


Fig. 2 Trend of CH_4 concentrations in ppb at Cape Meares, OR (45° N) (Khalil and Rasmussen, 1983)

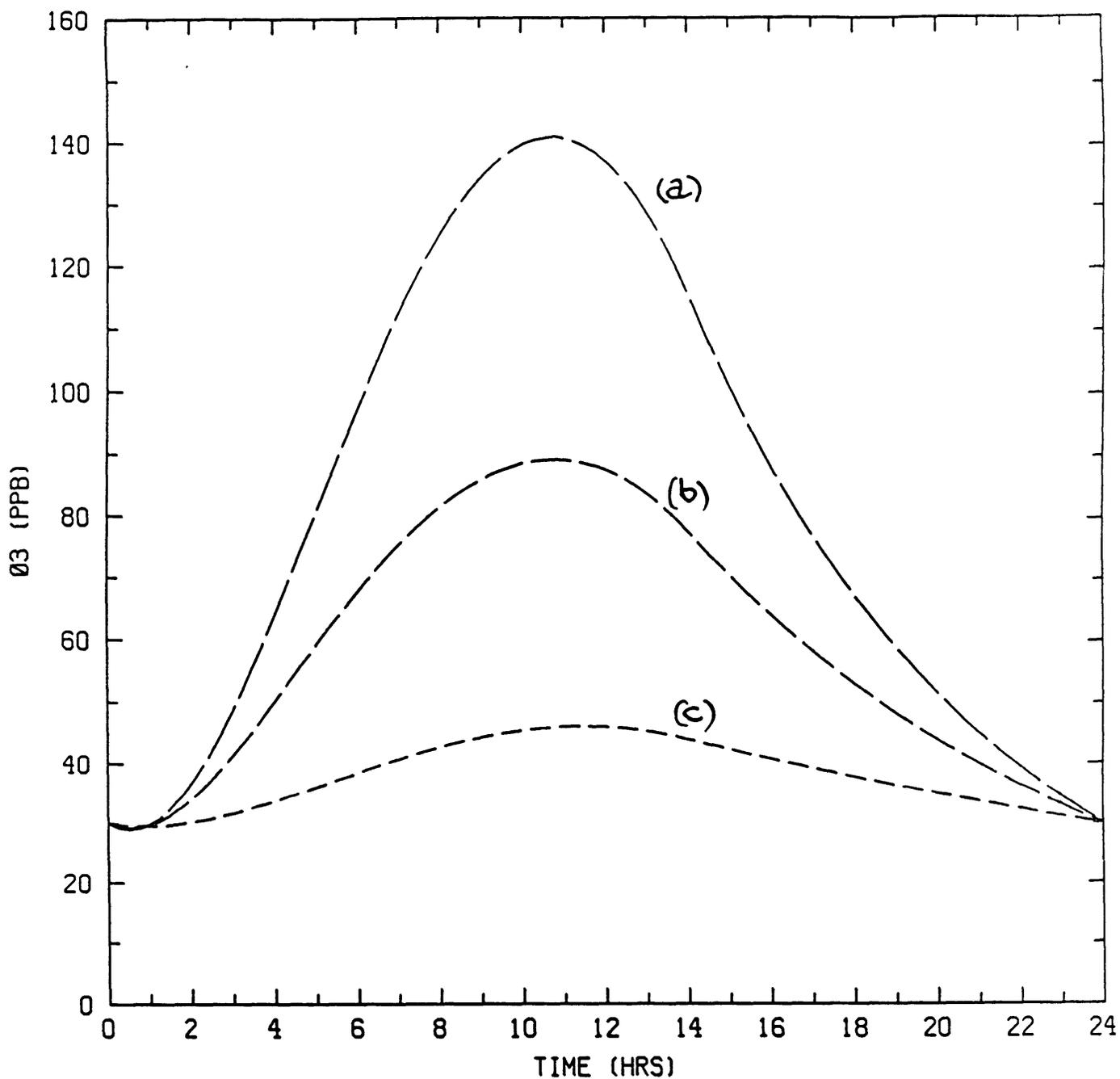


Fig. 3 Model results of diurnal O_3 concentrations in ppb
 (a) $k_3 [RO_2] = 0.2 \text{ s}^{-1}$; (b) 0.02 s^{-1} ; (c) 0.002 s^{-1} .
 Model parameters (see text) $[O_3]_0 = 30 \text{ ppb}$ $[NO_2]_0 = 10 \text{ ppb}$,
 $[NO]_0 = 0$, $k_1 = k_1' \sin \omega t$, $k_1' = 0.001 \text{ s}^{-1}$, $k_2 = 0.0004$
 $\text{ppb}^{-1} \text{ s}^{-1}$, k_4 automatically adjusts to give $[O_3]_{24h} = [O_3]_0$;
 sunrise at 0h, sunset at 14h.