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ATMOSPHERIC OXIDATION OF HYDROCARBONS

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Hydrocarbon oxidation in the atmosphere proceeds generally by the following sequence of reactions: hydrocarbon + OH → alkyl radical + H_2O, alkyl radical + $O_2(^3\Sigma)$ → alkylperoxy radical, alkylperoxy radical + NO → alkoxy radical + NO_2, alkoxy radical + $O_2(^3\Sigma)$ → aldehyde + HO_2. The atmospheric lifetimes of hydrocarbons are determined by their reactivity towards OH as well as by the average OH concentration level. They are compound specific and vary from several hours to several years. Hydrocarbon oxidation chains couple with other trace gases (O_x, HO_x and NO_x). For the conditions of the average continental atmosphere an increase of the oxidative potential (HO_x, O_x) is predicted through hydrocarbon oxidation.

KEY WORDS: atmospheric chemistry, hydrocarbon oxidation, free radicals, kinetics and mechanisms.

INTRODUCTION

Hydrocarbons are present in all parts of the atmosphere. In terms of individual compounds they represent the most diversified group of atmospheric trace gases with more than 500 identified compounds.[1] The simplest one of these, methane, is the most abundant hydrocarbon and is mixed fairly uniformly throughout the global troposphere with a mixing ratio of 1.6 ppm. All other hydrocarbons are less abundant and show more or less pronounced horizontal and vertical mixing ratio gradients.[2-6]

Hydrocarbons are generally reactive atmospheric constituents. Their reactivities and, as a consequence, their atmospheric residence times are compound specific and vary from as short as several hours for the most reactive olefins and aromatics to as long as about 10 years for CH_4.[7] Only the perhalogenated compounds, such as CCl_4 or the fluorochlorocarbons $CFCl_3$ and CF_2Cl_2, are essentially unreactive and infinitely stable in the troposphere.

The earth's atmosphere is oxidative in nature. As a consequence the oxidation of hydrocarbons provides important coupling mechanisms with other oxygen containing trace gas families (O_x, HO_x and NO_x). Moreover, although hydrocarbons are not generally considered as pollutants, their oxidation is responsible for the formation of secondary pollutants such as CO, O_3, PAN and aerosols.

Atmospheric oxidation of hydrocarbons is both initiated and continued by radical chemistry. Reactions between stable hydrocarbon species and O_2 are much too slow to create reasonable oxidation rates on a realistic time scale. This is true for both the gas phase and the condensed liquid phase, as represented in the atmosphere by clouds, fogs and rain drops. In this paper we will first present the mechanisms and kinetics of hydrocarbon oxidation and will then discuss how this oxidation couples with the

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level of HO_x. The latter is of particular importance since HO_x represents the oxidative potential of the atmosphere.

KINETICS AND MECHANISMS OF HYDROCARBON OXIDATION

The Tropospheric Photooxidation System

Hydrocarbon oxidation cannot be discussed with short prior reference to the photooxidation system which is responsible for its initiation. According to present day knowledge the most important species is the hydroxyl (OH) radical. It is formed by O_3 photolysis in the short wavelength cut-off region (λ = 295–305 nm) of solar radiation followed by the rapid reaction of the $O(^1D)$ photolysis product with H_2O, viz.

$$O(^1D) + H_2O \longrightarrow 2OH$$

Once OH is formed it undergoes a rapid cyclic transformation involving HO_2 and driven by CO and NO (Fig. 1). The strength of this recycling mechanism and hence the partitioning of HO_x between OH and HO_2 depends on the concentration levels of the species involved. Assuming typical tropospheric mixing ratios in continental air of $[O_3]$ = 50 ppb, [CO] = 1 ppm, [NO] = 1 ppb, $[H_2O] = 5 \times 10^{-3}$ as well as an O_3 photolysis frequency of $J_{O_3} = 1 \times 10^{-5}\,s^{-1}$, corresponding to a solar zenith angle of 20° we predict HO_x concentrations as shown in Fig. 2. This result[8] is obtained from a simple photochemical box model calculation with the integration of the rate equations carried out until steady state of the free radical concentrations is obtained.

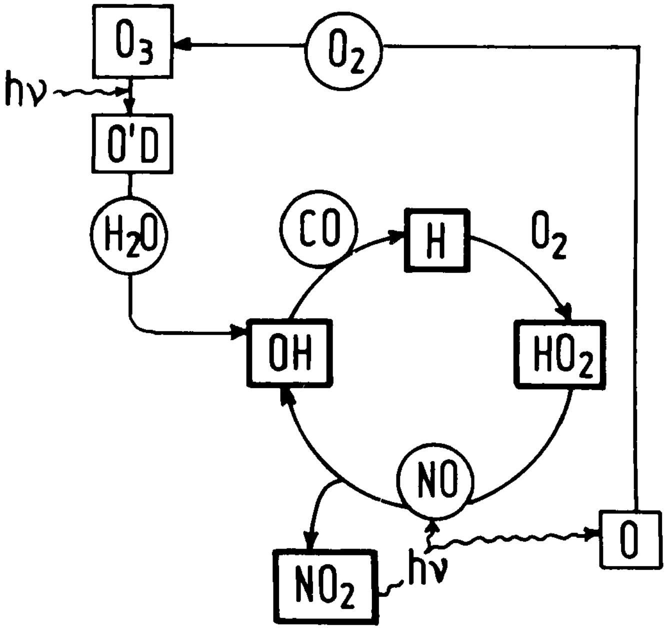


FIGURE 1 Main tropospheric cycle of HO_x.

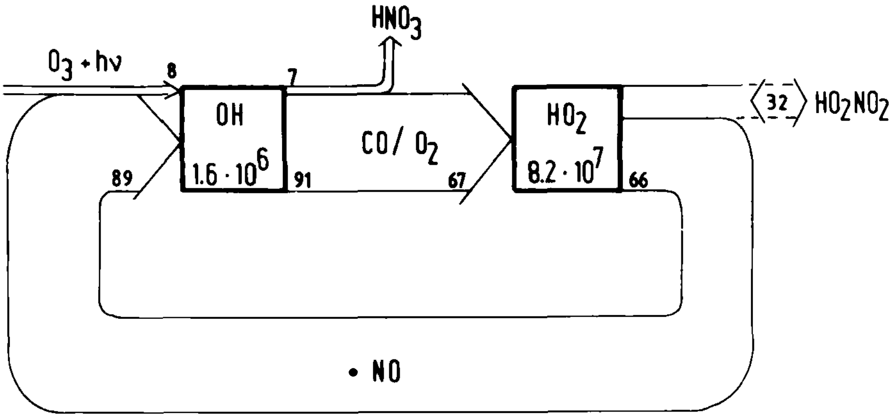


FIGURE 2 Tropospheric HO_x balance in continental air showing both steady state concentrations and fluxes.

As can be seen, [OH] at steady state is predicted to be $1.6 \times 10^6 \text{cm}^{-3}$, corresponding to a mixing ratio of as low as 6×10^{-14} (!) at STP. Moreover the calculated fluxes indicate that for these conditions by far most OH is a result of the recycling from HO_2 in reaction with NO.

Oxidation of Alkanes and Oxygenated Saturated Hydrocarbons

Although HO_2 is the more abundant of the HO_x species its reactivity towards all hydrocarbons is in generally very low and cannot compete with the OH radical. As a consequence reactions of the OH radical have been extensively studied in the laboratory and the results are well documented in a number of comprehensive reviews.[7,9,10] Rate coefficients for reactions of OH radicals with a number of selected alkanes and oxygenated hydrocarbons as well as the corresponding lifetimes of these compounds, are summarized in Table I. The latter are calculated from the relation $\tau = \{k_{OH}[\overline{OH}]\}^{-1}$, where $[\overline{OH}]$ is the diurnally and seasonally averaged tropospheric OH concentration, taken as $5 \times 10^5 \text{cm}^{-3}$.

The mechanism of the oxidation of alkanes is presented schematically in Fig. 3. The result of the initial attack of OH radicals is H atom abstraction and formation of an alkyl radical. The subsequent fate of alkyl radicals is predominantly a recombination with O_2 to form the alkylperoxy radical. This reaction is driven by the high recombination rate and the thermal stability of the peroxy radicals at ambient temperatures. In addition to recombination there is also a minor pathway to yield alkene + HO_2. In terms of total yield, however, this route does not seem to be a significant source of atmospheric alkenes.

The oxidation of alkanes would essentially stop at the peroxy level were it not that the atmosphere, and in particular the continental troposphere, contains NO_x. In the presence of NO alkylperoxy radicals are rapidly reduced to the corresponding oxy radicals. Simultaneously, NO is oxidized to NO_2. The subsequent fate of oxy radicals, however, is more diverse than that of peroxy radicals. The dominant loss process is again a reaction with O_2 leading to the formation of an aldehyde + HO_2. However, oxy radicals can also decompose to yield R + CH_2O or be stabilized by internal H-atom migration. In the latter case a hydroxyalkyl radical is formed.

TABLE I

Rate coefficients at 298 K for reactions of OH radicals with and atmospheric lifetimes of selected alkanes and oxygenated hydrocarbons

Compound	k_{OH}^{298K}/cm^3 · molecule^{-1} s^{-1}	$\tau^{i)}$
CH_4	8.9×10^{-15}	7.1 y
C_2H_6	2.7×10^{-13}	86 d
C_3H_8	1.6×10^{-12}	14 d
n-butane	2.7×10^{-12}	8.6 d
i-butane	2.5×10^{-12}	9.2 d
n-pentane	3.7×10^{-12}	6.2 d
cyclo-pentane	4.7×10^{-12}	4.9 d
2,3-dimethyl-butane	4.8×10^{-12}	4.8 d
2,2,4-trimethyl-pentane	3.7×10^{-12}	6.2 d
n-octane	8.4×10^{-12}	2.7 d
formaldehyde	9.4×10^{-12}	2.5 d$^{ii)}$
acetaldehyde	1.2×10^{-11}	1.9 d
acetone	2.2×10^{-12}	105 d
2-butanone	1.4×10^{-12}	16 d
methanol	8.0×10^{-13}	29 d
ethanol	2.9×10^{-12}	8.0 d
n-propanol	4.8×10^{-12}	4.8 d
ethylenglycol	7.7×10^{-12}	3.0 d

i) Based on an assumed average tropospheric OH concentration of 5×10^5 cm^{-3}.

ii) Partial lifetime with respect to reaction with OH. The real lifetime is determined by photolysis and is ~ 15 hours.

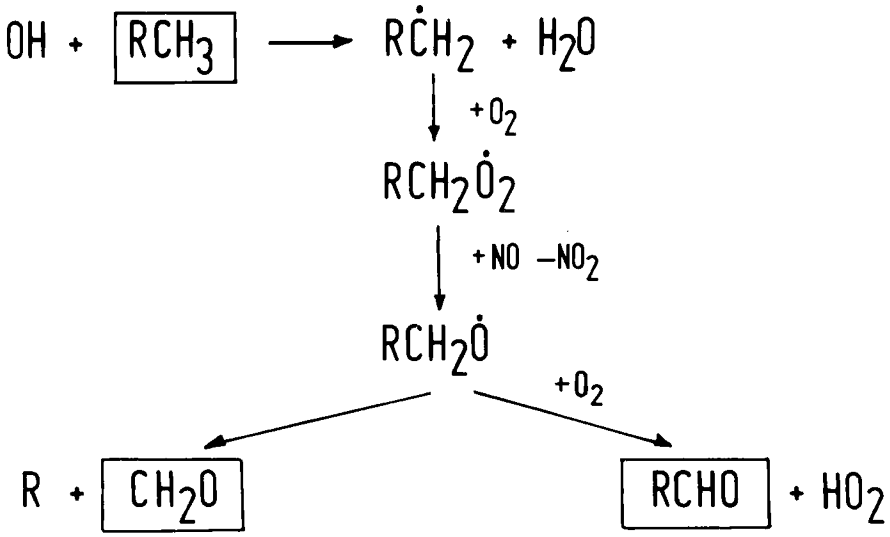
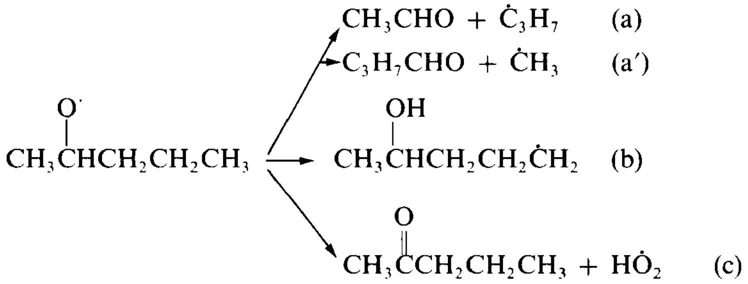


FIGURE 3 Tropospheric oxidation pathway of alkanes.

Quantitative experimental evidence for the various reaction channels of oxy radicals is still relatively scarce. Moreover, even for the simplest oxy radical that occurs in the CH_4 oxidation chain (methoxy, CH_3O), for which only the O_2 reaction is possible, we have recently shown that $CH_2O + HO_2$ only account for 85% of the products.[11] The energetics of the apparently simple $CH_3O + O_2$ reaction appears to be much more complex and products like HCOO (formoxy) + H_2O are suggested as alternatives.[12] Whereas for $\leqslant C_3$-alkoxy radicals the O_2 reaction always seems to dominate[13,14] unimolecular processes become important in larger radicals.



For instance, for the 2-pentoxy radical with the reaction possibilities the isomerization channel (b) is expected to account for ~ 75% at 298 K in 1 atm of air.[13,15] Relative to the O_2 reaction (c) (~ 24%) the decomposition channels (a, a') leading directly to aledhyde formation are probably of minor ($\leqslant 1\%$) importance.

A question of general importance to the oxidation route and hence the final products of any hydrocarbon is the site of the primary OH attack. C–H bonds are not equivalent and of different strength. As a consequence in any H abstraction reaction by OH radicals there is a dynamic propensity to favour the formation of the thermodynamically most stable radical. From measurements of rate coefficients for a large series of alkanes and oxygenated saturated hydrocarbons we have found the simple relation

$$\log(k/n) = (9.4 \pm 1.6) - (0.23 \pm 0.02) \cdot \mathrm{BDE}$$

where BDE is the bond dissociation energy in kcal/mol of the weakest C–H bond and n is the number of equivalent H atoms with this bond energy. This relation predicts that the reactivity towards OH increases by roughly an order of magnitude for a decrease in bond energy by 5 kcal/mol. Moreover, both semi-empirical[16] and empirical[10] methods have been devised to predict site-specific and overall rate coefficients from known or estimated C–H bond energies[16] and substituent effects in primary, secondary and tertiary carbon atoms,[10] respectively. From these the following scale of decreasing reactivity can be deduced: $-O-C\underline{H}_2- > HO-C\underline{H}_2- > -C(O)O-CH_2- \sim -CH_2-C\underline{H}_2- > CH_3-C\underline{H}_2- > -CH_3 \gtrsim -O\underline{H}$. Hence, the highest reactivity is found for the α–CH_2 group in ethers; H-atom abstraction from terminal OH or CH_3 groups is relatively unimportant.[17]

The perhaps most important group among the oxygenated hydrocarbons in the atmosphere are aldehydes. As has been shown above they are the intermediate products of any hydrocarbon oxidation. The simplest one of these, formaldehyde, results from methane and also occurs as a product of the oxidation of terminal alkenes such as propene (see below) and 1-butene. Formaldehyde is degraded by reaction with OH and also by photolysis, viz:

$$CH_2O + OH \longrightarrow HCO + H_2O \quad \text{(d)}$$

$$CH_2O + h\nu \longrightarrow HCO + H \quad \text{(e)} \ \phi = 0.4$$

$$\longrightarrow CO + H_2 \quad \text{(e}') \ \phi' = 0.6$$

with the relative contribution (d)/(e) + (e′) $\simeq$ 0.5 in the global troposphere.[18] Because of the fast consecutive reaction $HCO + O_2 \rightarrow CO + HO_2$ the only stable carbon containing product is CO. However, there is an important difference between the OH and the photon-induced degradation channels with respect to the coupling with HO_x: Whereas (d) does not change HO_x, channel (e) is a net source of HO_x (see below).

For larger aldehydes photolysis is no longer important and the OH reaction is dominant. Fig. 4 summarizes the tropospheric oxidation pathway of acetaldehyde. Because of the low aldehyde-C–H bond energy, the only primary product is the acetyl radical which in the presence of O_2 forms acetylperoxy. The subsequent degradation of $CH_3C(O)OO$ is again by interaction with NO_x. However, unlike alkylperoxy radicals which only react with NO, acetylperoxy also reacts with NO_2 to form peroxyacetylnitrate (PAN). It has recently been shown[19] that PAN is not easily water soluble and also relatively stable against photodecomposition. Its primary fate therefore is the reverse decomposition into acetylperoxy + NO_2 for which a lifetime in the lower troposphere of ~3 h has been estimated.[19]

Oxidation of Alkenes and Aromatics

Unlike alkanes the atmospheric oxidation of alkenes and aromatics is initiated not by H atom abstraction but by OH addition to the unsaturated π-system. Rate coefficients for this process and corresponding lifetimes of a number of selected compounds are summarized in Table II. Addition rather than abstraction is caused because olefin and aromatic H atoms are too strongly bound and OH is generally an electrophilic reagent. As a consequence the addition rate coefficients for a homologous series of alkenes or aromatics can be correlated with the ionization potential[20,21] and/or the overall electrophilic substituent constants.[10,22]

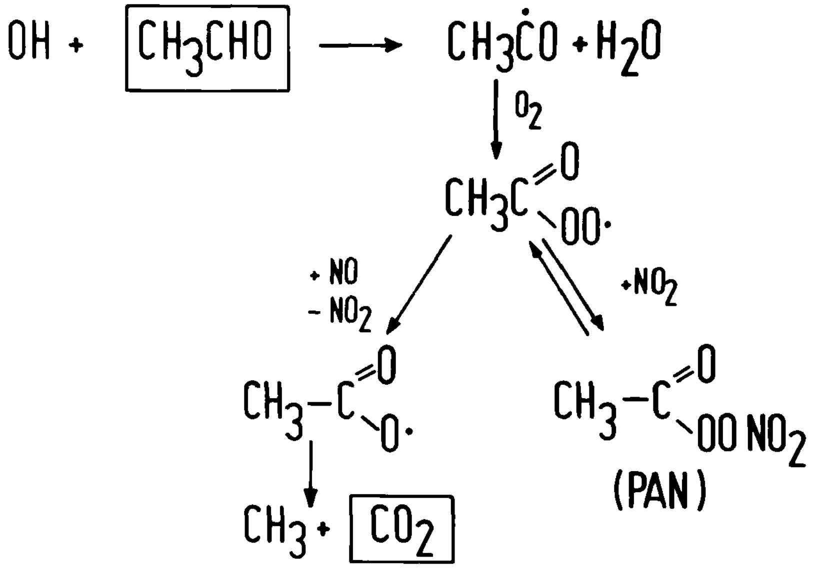


FIGURE 4 Tropospheric oxidation pathway of acetaldehyde.

TABLE II

Rate coefficients at 298 K and 1 atm pressure for reactions of OH radicals with and atmospheric lifetimes of selected alkenes and aromatics

Compound	k_{OH}^{298}/cm^3 molecule^{-1} s^{-1}	$\tau^{i)}$
ethene	5.3×10^{-12}	4.3 d
propene	2.0×10^{-11}	27 h
1-butene	3.8×10^{-11}	14 h
i-butene	5.0×10^{-11}	11 h
cis-2-butene	5.3×10^{-11}	10.5 h
1,3-butadiene	6.5×10^{-11}	8.5 h
3-methyl-1-butene	3.1×10^{-11}	18 h
1-hexene	3.1×10^{-11}	18 h
benzene	1.1×10^{-12}	21 d
toluene	6.4×10^{-12}	3.6 d
phenol	2.8×10^{-11}	19 h
ethylbenzene	7.9×10^{-12}	2.9 d
o-xylene	1.4×10^{-11}	1.6 d
1,2,3-trimethyl-benzene	3.3×10^{-11}	17 h
methoxybenzene	1.9×10^{-11}	1.2 d
aniline	1.2×10^{-11}	1.9 d
nitrobenzene	2.1×10^{-13}	3.6 m
chlorobenzene	6.7×10^{-13}	34 d
naphthalene	1.5×10^{-11}	1.5 d

i) Based on an assumed average tropospheric OH concentration of 5×10^5 cm^{-3}.

The atmospheric degradation pathway of propene is presented schematically in Fig. 5. The joint result of OH addition, recombination with O_2 and reaction with NO is the formation of a β-hydroxy-alkoxy radical. As for the alkoxy radicals formed from the alkanes this radical has various reaction routes. Whereas in the former case, however, the O_2 reaction dominates, this is not observed for the β-hydroxy-alkoxy radicals.[13,23] Here, the decomposition forming an aldehyde + hydroxyalkyl radical is the dominant reaction route. Since the latter rapidly reacts with O_2 to form a second aldehyde, the net overall result is the oxidative split of the double bond producing two aldehyde fragments. A small fraction of the β-hydroxy-alkoxy radicals can also recombine with NO_2 to form β-hydroxy-alkyl nitrate. No conclusive experimental evidence has, however, so far been presented for this route. It should be noted that the primary OH addition can of course be terminal (as show in Fig. 5) or central. For propene the relative contributions are 65 vs. 35%.[10] The final products resulting from both routes are identical.

The addition of OH radicals to aromatic compounds results in the formation of a substituted hydroxy-cyclohexadienyl-radical. For the case of benzene this radical has recently been directly detected in the gas phase.[24,25] The subsequent reaction is again expected to be with O_2, with the addition (to form the substituted hydroxy-cyclohexadienylperoxy radical) dominating H-atom abstraction. This is evidenced by the relatively small yield of cresols ($\leqslant$ 16%) observed in the photooxidation of toluene[26–28] as opposed to carbonyl compounds postulated to arise from ring cleavage.[29] This ring cleavage is expected to occur from the oxy radical formed in reaction of the hydroxy-cyclohexadienylperoxy radical with NO. The postulated atmospheric degradation pathway of toluene is presented in Fig. 6. It should be noted that primary H-abstraction from the CH_3 group in toluene only occurs to an extent of ~ 16%[9] relative to OH addition. The product of this route is benzaldehyde.

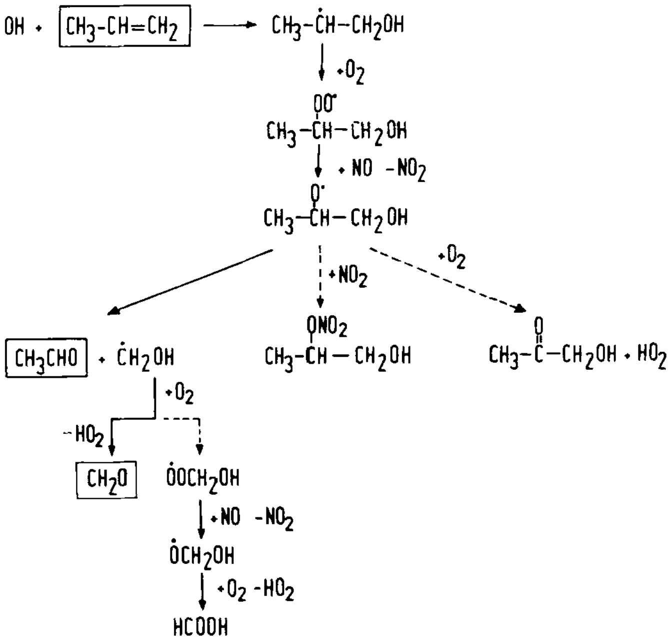


FIGURE 5 Atmospheric degradation route of propene.

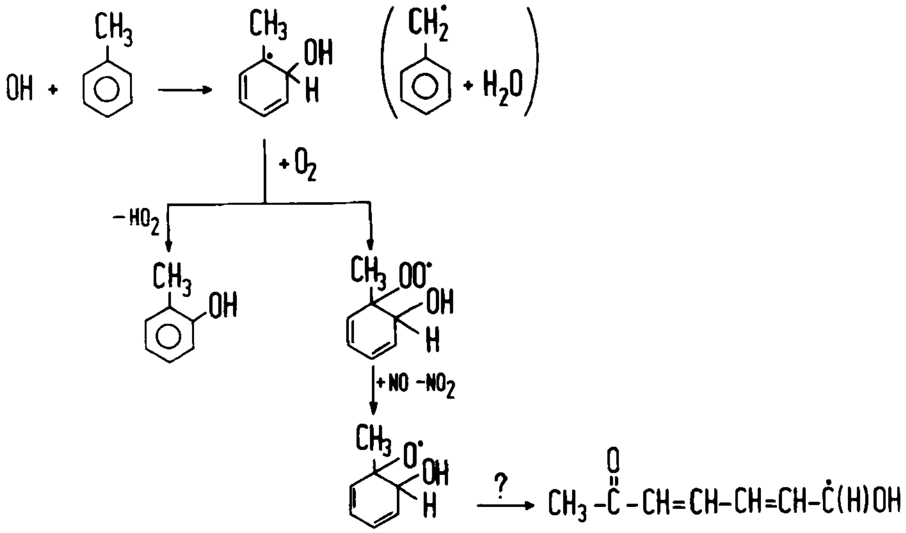


FIGURE 6 Assumed atmospheric degradation route of toluene.

DISCUSSION

The atmospheric oxidation of hydrocarbons is well investigated in its basic principles. As a result of a number of direct and indirect laboratory photooxidation studies there is convincing evidence that the atmospheric degradation of hydrocarbons proceeds in the sequence: hydrocarbon–carbon centered (alkyl) radical–oxygen centered (peroxy) radical–oxy radical–aldehyde, where the reagents in the same sequence are OH, O_2, NO, O_2. Aldehydes are subsequently oxidized to CO and CO_2. Alcohols and acids do not occur in the standard atmospheric oxidation chain. However, organic acids are observed in tropospheric air and in rain[30,31] and their formation mechanisms need yet to be satisfactorily explained. Moreover, there is insufficient knowledge about the interaction of hydrocarbon oxidation with NO_2, in particular with respect to the formation of nitrates. Some of these have a relatively high thermal stability and hence serve as reservoir species of hydrocarbon oxidation intermediates and of NO_2, especially at the low temperatures of the upper troposphere. Finally, the oxidation of hydrocarbons at low NO_x levels (as typical for the free marine troposphere) contains a number of new features characterized by peroxy–peroxy radical interactions. Rates and products for these reactions are in general not yet well-known.[32]

Hydrocarbon oxidation in the atmosphere is not only of interest as a degradation mechanism of organic compounds, it is also of importance to the global tropospheric oxidative potential. This is because any hydrocarbon oxidation chain couples with the photooxidation system, notably HO_x. The nature of this coupling is shown schematically in Fig. 7, where we present the consumption of OH and the formation of HO_2 for

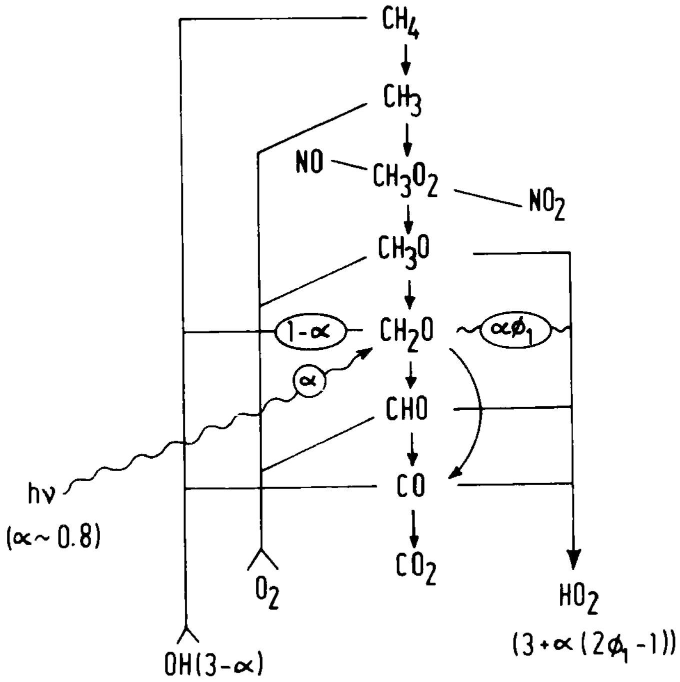


FIGURE 7 Basic tropospheric CH_4 oxidation scheme and net HO_x balance.

the complete oxidation chain of methane. As can be seen, despite the fact that OH is consumed in reactions with CH_4, CH_2O and CO, there is a net gain of $2 \cdot \alpha \cdot \phi \simeq 0.6$ moles of HO_x per mole of CH_4 oxidized. In here α and ϕ is the fraction of CH_2O that is degraded by photolysis and the quantum yield for radical products, respectively. Moreover, since any HO_2 formed will rapidly oxidize NO to NO_2 which is then followed by photodissociation of NO_2, viz.

$$HO_2 + NO \longrightarrow OH + NO_2$$

$$NO_2 + \hbar\nu \longrightarrow NO + O$$

there is also a net gain of 3.8 moles of O_x. As a consequence CH_4 oxidation increases the oxidative potential of the atmosphere.[8,33] This effect applies to the continental atmosphere with relatively high NO_x levels. At low $[NO_x]$ the effect is reduced and can also change its sign.[8,33]

Net HO_x formation in hydrocarbon oxidation only occurs from CH_2O photodissociation. Since CH_2O is also an intermediate in the oxidative breakdown of any hydrocarbon, the arguments presented above also apply to larger hydrocarbons. However, there may be a delaying effect on photostationary state of HO_x due to the fact that CH_2O formation (and hence HO_x formation) and initial OH loss do not occur on the same time scale.

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