On the role of OH and HO_2 radicals in the troposphere

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ABSTRACT

According to a photochemical model proposed by Levy, the effective number densities of hydroxyl radicals in the troposphere are of the order of 2.5×10^6 molecules cm^3. It is shown here that such high OH number densities are inconsistent with two independent sets of observational data: The distribution of CO mixing ratios with latitude in the northern and southern hemisphere; and with the rate of nitrate precipitation in the northern hemisphere. The upper limit of the effective OH number density suggested by the observations is at the most one fifth of that predicted by Levy. It appears that the reconversion of HO_2 to OH radicals is not as effective as assumed in the model. Calculations are presented for the loss of radicals to aerosol particles. It is shown that aerosol scavenging of OH radicals is negligible compared to consumption by gas reactions, but that aerosol scavenging of HO_2 radicals might provide an important loss process for this species.

Introduction

Since the time when Chapman (1930) first interpreted the earth's ozone layer in terms of the oxygen photo-dissociation mechanism, free radicals—i.e. neutral fragments of molecules—have played a leading part in atmospheric chemistry. Until recently, the upper atmosphere, including the stratosphere has been considered the principal domain of atmospheric radical chemistry. Levy (1971, 1972, 1973) has now demonstrated on the basis of plausible photochemical reaction mechanisms that radical reactions are important also in the troposphere. Thus, in the production and loss of specific trace gases, radical reactions are postulated to compete with other types of sources and sinks such as precipitation and microbiology. The effect of radical reactions in the chemistry of air pollution, specifically photochemical smog, has been recognized for some time (Leighton, 1961).

In unpolluted tropospheric air, the most important radicals appear to be OH and HO_2, because they are essentially inert towards the main atmospheric constituents N_2, O_2, Ar, CO_2 and H_2O, but react readily with many trace gases. In particular, the reaction of OH with methane has been pronounced a significant source of atmospheric carbon monoxide (Levy, 1972, 1973; McConnell et al., 1971) and the reaction of OH with nitrogen dioxide, a significant source of nitric acid (Levy, 1973). These two processes are singled out for discussion in the present paper. The recent measurements by Seiler (1974) of CO mixing ratios in air over the northern and southern Atlantic ocean provides an upper limit estimate of the amount of CO produced by oxidation of atmospheric methane, when compared to that produced by anthropogenic sources located predominantly in the northern hemisphere. Extensive data on nitrate precipitation over the continents in the northern hemisphere are also available to permit an upper limit estimate of nitric acid production via the reaction of OH with nitrogen dioxide. Both estimates turn out to be lower than the corresponding production rates predicted on the basis of effective OH number densities derived by Levy (1973). It appears that the calculated OH number densities are too high and that Levy's model must be modified to include additional loss processes either for OH or HO_2. One type of process dismissed by Levy (1971) is the scavenging of radicals by aerosol particles. Loss of radicals by collision with aerosol particles is also investigated in the

Table 1. *Rates of OH radical reactions with atmospheric trace gases at 2 km altitude*

Trace gas	Mixing ratios[a] (ppbv)	Rate coeff.[b] (cm^3 sec)	Rate (sec^{-1})
CH_4	1 500	5.0^{-15c}	1.7^{-1c}
CO	100	1.0^{-13}	2.0^{-1}
H_2	500	4.2^{-15}	4.3^{-2}
H_2CO	~1	1.5^{-11}	3.0^{-1}
NO_2	2	5.0^{-12}	2.0^{-1}
NO (noontime)	1	1.5^{-12}	3.0^{-2}
SO_2	2	Unknown	—
NH_3	0.5	1.5^{-13}	1.5^{-3}
C_2H_4	~0.06	2.4^{-12}	3.0^{-3}
C_2H_{10}	~0.07	1.8^{-12}	2.6^{-3}
H_2O_2	0.1	7.0^{-13}	1.5^{-3}

[a] Author's estimate from various sources.
[b] Values taken from Levy (1972, 1973).
[c] Superscripts designate powers of ten.

present paper. It is confirmed that for OH radicals aerosol scavenging is negligible compared with loss due to reactions in the gas phase. Currently known gas reactions of HO_2 radicals are less rapid, however, so that for these species aerosol scavenging might well provide a competitive loss process.

Sources and sinks of OH and HO_2 in the troposphere

As a background for the subsequent discussion of the reactions of OH radicals with methane and nitrogen dioxide a brief outline of the sources and sinks of OH and HO_2 as postulated by Levy (1971, 1972, 1973) will be given. The major source of OH in the lower troposphere is the reaction of water vapor with $O(^1D)$. This species is produced by the photolysis of ozone (Schiff, 1972) in the long-wavelength tail of the Hartley band that penetrates the u.v. absorbing ozone layer in the stratosphere. Most of the $O(^1D)$ atoms thus generated are converted to ground state O-atoms by deactivating collisions with nitrogen and oxygen. A few percent (between 1 and 10%) react with water vapor:

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$$

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2$$

$$O(^1D) + H_2O \rightarrow OH + OH$$

Loss of OH is due to reactions with a great variety of atmospheric trace gases. Table 1 lists known trace gases, their estimated mixing ratios, the appropriate rate coefficients and the resulting OH loss rates. The reactions with methane, carbon monoxide, formaldehyde and nitrogen dioxide predominate. With exception of the reaction with NO_2 which is an attachment reaction to be discussed later, the interaction of OH with these trace gases leads to the production of new hydrogenous radicals. The individual reaction sequences will not be reviewed here (see Levy, 1972, 1973 for details) but it is important to note that in general the consumption of an OH radical sooner or later results in the formation of a hydrogen peroxy radical HO_2. A simple example is provided by the reaction of OH with CO:

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

where M represents any suitable third body.

Table 2 displays our present knowledge—respectively ignorance—of the reactivity of HO_2 radicals towards the same trace gases as listed in Table 1. The most prominent reaction currently known occurs with nitric oxide which during the day is present in the atmosphere on account of the photolysis of NO_2. The importance of this reaction

$$HO_2 + NO \rightarrow NO_2 + OH$$

Table 2. *Rates of HO_2 radical reactions with atmospheric trace gases at 2 km altitude*

Trace gas	Mixing ratio[a] (ppbv)	Rate coeff.[b] (cm^3 sec)	Rate (sec^{-1})
CH_4	1 500	Nil	—
CO	100	$< 1.5^{-20c}$	—
H_2	500	Nil	—
H_2CO	~1	Unknown	—
NO_2	2	Unknown	—
NO (noontime)	1	$\sim 5.0^{-13}$	1.0^{-2}
SO_2	2	$\sim 5.0^{-16}$	2.0^{-5}
NH_3	0.5	Unknown	—
C_2H_4	0.06	Unknown	—
C_2H_{10}	0.07	Unknown	—
H_2O_2	0.1	—	—

[a] Author's estimate from various sources.
[b] Values taken from Davis et al. (1973).
[c] Superscripts designate powers of ten.

lies in the regeneration of hydroxyl radicals. In this manner a chain mechanism is set up leading to a considerable increase of the steady state OH concentration compared to that established on the basis of the direct photochemical production of OH by $O(^1D)$ alone. According to Levy (1973) and McConnell et al. (1971) who consider a similar model, noon time OH number densities in the lower strata of the troposphere reach values of about 10^7 molecules cm^3. The daily average amounts to about 2×10^6 molecules cm^3. At higher altitudes, in the vicinity of the tropopause, the corresponding OH number densities are about a factor of 3 lower. In the absence of the HO_2 recycling reaction, these OH number densities would be by about a factor of ten lower.

CO production and loss

An important consequence of the presence of OH radicals in the troposphere is their reaction with methane. The predicted OH number densities oxidize methane at a rate of 2×10^{11} molecules/cm^2 sec (Levy, 1972, 1973; McConnell et al., 1971). The resulting major carbonaceous product, carbon monoxide, is again oxidized mainly by OH radicals. In the steady state, the concentration ratio CO/CH_4 is given by the ratio of the rate coefficients associated with both processes, suitably averaged over the vertical temperature profile. For an unperturbed atmosphere, taking a CH_4 mixing ratio of 1.5 ppmv, one calculates for CO a mixing ratio of 0.06 ppmv and a chemical life time of 0.1 years. In the southern hemisphere which is affected little by man-made CO sources, the measurements by Seiler (1973) over the Atlantic ocean indicate CO mixing ratios of 0.05 ppmv in close agreement with the calculated value. In the northern hemisphere, however, the situation is different. The average CO mixing ratio is about 0.15 ppmv and a concentration gradient is observed in the direction of decreasing latitude. Even the equatorial region of the southern hemisphere is affected by the concentration gradient. These features require a CO source localized mainly in the 50°–70° N latitude belt and operative in addition to the uniform production from methane. According to present knowledge, the additional source can be identified only with the anthropogenic source, as other natural sources of sufficient strength are not known (Seiler, 1973). The higher CO mixing ratios in the northern hemisphere compared with the southern hemisphere indicate that the additional CO source in the north should have at least the magnitude of the natural source. However, even the most recent up-grading of the anthropogenic CO source strength to 400 million tons year, corresponding to about 1×10^{11} molecules cm^2 sec (Jaffe, 1972) does not yet make it sufficiently competitive with the production of CO from methane as calculated by Levy. Hence, it appears that the latter source must be smaller than predicted. The same conclusion can be derived from the latitudinal concentration profile in a somewhat different manner. The chemical life time of 0.1 years obtained by Levy for the natural life time of CO is shorter than the time required for transport of CO rich air across a 45° latitude belt, which can be estimated as about 0.25 years on the basis of an average meridional eddy diffusion coefficient of 2×10^{10} cm^2 sec (Bolin & Keeling, 1963; Newell et al., 1969) for the tropical region. If the natural life time of CO were not greater than 0.1 years, the high CO mixing ratios in air at middle latitudes in the northern hemisphere should have decayed to values below 0.1 ppmv by the time this air reaches the interhemispheric conversion zone. This behavior is in contrast to observation, so that a longer CO life time is required. Seiler (1973) estimates from a variety of data independent of the CO source from methane an atmospheric CO life time of 0.5 ± 0.2 years. A life time of this magnitude would require a five-fold reduction of effective OH number densities from those predicted by Levy (1973) if one assumes that OH radicals remain the major sink for carbon-monoxide.

Rate of nitrate precipitation

The formation of nitric acid by OH radicals occurs via the association reaction

$$OH + NO_2 \rightarrow HNO_3$$

At low pressures the reaction is a three body process, whereas at atmospheric pressures it has almost reached the high pressure second order limit. Morley & Smith (1972) estimate from laboratory data at pressures up to 300 Torr a rate coefficient at 750 Torr of about 10^{-11} cm^3/molecule sec. We have used the more conserva-

Table 3. *Comparison of NO_3^- deposition and HNO_3^- production from $OH + NO_2$*

Constituent	Over continents	Over oceans
Concentration NO_2 gasphase	4 ppb at ground 2 ppb above 2 km	1 ppb
NO_3^- precipitated	~ 1 mg/l	$\leqslant 0.15$ mg/l
Production rate HNO_3 gas phase	2.1×10^{11} molecules/cm² sec	8.6×10^{10} molecules/cm² sec
Deposition rate of NO_3^-	2.6×10^{10} molecules/cm² sec	$\leqslant 4.0 \times 10^{9}$ molecules/cm² sec

tive value of 5×10^{-12} cm³/molecule sec determined by Simonaitis and Heicklen (1972) and employed by Levy (1973). For an estimate of the rate of HNO_3 production by this process the concentration of nitrogen dioxide in the atmosphere must be known. Since the sources of NO_2 even in unpolluted areas occur all on land, its concentration is highest in surface air over the continents, decreases with altitude and is lowest over the oceans. For continental surface air, the estimate of 4 ppbv by Robinson & Robbins (1970) is adopted here. The average altitude profiles obtained over Europe by Georgii & Jost (1964) indicate that above 2 km altitude the NO_2 mixing ratio is practically constant at 2 ppbv. Over the oceans the mixing ratio of NO_2 is probably latitude dependent similar to the mixing ratio of SO_2 (Georgii, 1970). We assume here an average NO_2 mixing ratio of 1 ppbv independent of altitude, somewhat higher than the estimate by Robinson & Robbins (1970) for that region. All these data refer to the northern hemisphere, as similar data for the southern hemisphere are not available. Utilizing these data in conjunction with the average OH number densities calculated by Levy (1973) for the tropospheric altitude regime leads to a production rate for HNO_3 of 2.1×10^{11} molecules/cm² sec over land, and 8.6×10^{10} molecules/cm² sec over the oceans. The first of these values agrees well with that derived by Levy (1973) himself.

Presently known removal processes for HNO_3 vapor in the troposphere include reaction with OH radicals, photolysis, and attachment to aerosol. The latter process dominates as can be illustrated by a comparison of HNO_3 life times associated with each of the three loss processes at 2 km altitude:

$$HNO_3 + OH \rightarrow H_2O + NO_3 \qquad \tau \approx 9 \times 10^5 \text{ sec}$$
$$HNO_3 + h\nu \rightarrow OH + NO_2 \qquad \tau \approx 1 \times 10^6 \text{ sec}$$
$$HNO_3 + \text{aerosol} \rightarrow \text{nitrate} \qquad \tau \approx 1 \times 10^2 \text{ sec}$$

Data for the rate coefficients and OH number densities required to estimate the time constants of the first two processes were taken from Levy (1973). The time constant for the attachment of HNO_3 to background aerosol was obtained with the assumption that each collision is effective. The collision rate derived in the next section was employed. Owing to the high cation content of aerosol the assumption that nitric acid is converted to nitrate upon each collision with aerosol is probably justified. However, scavenging by aerosol would remain the dominant loss process even if the aerosol attachment efficiency of HNO_3 were appreciably smaller than unity.

The predominant fate of aerosol particles is removal by precipitation (Junge, 1963). Hence, essentially all of the nitric acid produced in the troposphere will be removed as nitrate in precipitation, and the amount of precipitated NO_3^- multiplied with the mean rate of precipitation is a direct measure for the rate of atmospheric nitric acid formation, provided other sources of nitrate are negligible. Data on the amount of nitrate in precipitation have been assembled by Erikson (1952) for Europe, Junge (1958) for the Northamerican continent and Petrenchuk & Seleznewa (1970) for the Soviet Union. Although the data clearly exhibit the influence of seasons and local atmospheric dynamics, they are in accord with an approximate average of 1 mg/l nitrate in precipitation in the middle latitude belt of the northern hemisphere continents. The mean annual amount of precipitation in this region is about 800 mm or 0.08 liter/cm² (Sellers, 1965) so that the average flux of nitrate over land is 2.6×10^{10} molecules/cm² sec. Over the oceans the nitrate content of precipitation is less than 0.15 mg/liter (see for example Erikson, 1957 and Junge, 1958) so that the flux of nitrate is at the most 4×10^9 molecules/cm² sec.

These results are summarized in Table 3.

The comparison of predicted and observed nitrate precipitation rates indicates clearly that the observed values are by a factor of ten lower than the predicted ones. Despite the large fluctuations inherent in the observed nitrate precipitation it is considered unlikely that the error exceeds a factor of two. Similarly, the NO_2 measurements make it rather improbable that the employed NO_2 mixing ratios are as much as a factor of two too low, except perhaps over the oceans. Consequently, the discrepancy must be caused by the high values of OH number densities. This result is in accordance with the conclusion derived from discussing the CO concentration measurements in the preceding section. A tenfold reduction of the OH number densities given by Levy would lead to a better agreement with observations.

It should be emphasized that the observational data on which this conclusion is based refer all to the northern hemisphere. At the present time the observational data in the southern hemisphere are too fragmentary to permit a similar analysis for that part of the globe. Differences in the concentration of several important trace gases (e.g. CO) may well cause the average OH number density in the southern hemisphere to differ from those in the north. Hence, we cannot simply extrapolate the above result for the OH number density in the northern hemisphere to the southern hemisphere and must leave this question open for future investigations.

Loss of radicals to aerosol

The realization that at least in the northern hemisphere the effective OH number densities are smaller than predicted on the basis of Levy's model requires a re-assessment of the important factors entering into the computation of the OH concentration. Among these factors, the direct production of OH via the reaction of $O(^1D)$ depends on radiation densities and $O(^1D)$ quantum yields from O_3 photolysis in the 300–350 mμ wavelength region. The radiation density is computed from the known extraterrestrial radiation flux and is probably reasonably correct; the $O(^1D)$ quantum yield is experimentally still not too well established (Schiff, 1972) but Levy (1972, 1973) states that he has used conservative values. Other factors are rate coefficients and trace gas concentrations for OH loss reactions. These are reasonably well known (see Table 1), and additional inconvertible loss of OH by gas phase reactions is not readily conceivable. The only important factor left, the effectiveness of recycling HO_2 radicals as a second source of OH, depends strongly on the loss of HO_2 radicals by other channels. Currently, little is known about such loss reactions in the gas phase. It is the purpose of this section to show that scavenging by aerosol may serve as an important loss channel for hydrogen peroxy radicals.

In calculating collision rates of molecules with atmospheric aerosol particles, three types of aerosols must be considered: (*a*) background aerosol, (*b*) maritime aerosol, and (*c*) continental aerosol (Inadvertent Climate Modification, Report of the Study of Man's Impact on Climate, 1971, Junge & Jaenicke, 1971). Background aerosol exists in the entire troposphere. We adopt particle densities of 400 cm^{-3} near the ground, decreasing with altitude proportionally with the atmospheric density. Maritime and continental aerosols are confined to the lower strata of the troposphere. In all cases, size distributions are approximately known. They range from 5×10^{-3} to 100 μm (radius). The sea spray aerosol adds comparatively little to the background aerosol and affects mainly the size range 1–10 μm, where the concentration of background aerosol is at least two orders of magnitude lower than at the maximum at about 0.1 μm. Accordingly, the maritime aerosol contribution is neglected for the present purpose. The continental aerosol, by contrast, features a size distribution similar to that of background aerosol with a maximum concentration higher by almost two orders of magnitude. We adopt a particle density of 10^4 cm^{-3} near the ground, decreasing with a scale height of $h = 1$ km, until above 5 km altitude it blends with the background particle density.

Aerosol particles are assumed to consist of concentrated solution droplets of radius r. In the literature the size distribution is usually given by a distribution function $f(r)$ such that the number density of aerosol particles falling into the size range between r and $r + dr$ is defined as

$$dN(r) = f(r)\, d\log r = f(r)\, dr/r \log 10 \qquad (1)$$

In the lowest size range, the mean free path of molecules exceeds the size of an aerosol par-

Table 4. *Time constants in seconds for loss of OH and HO_2 radicals by interactions with trace gases and by collisions with aerosols and cloud elements in the troposphere*

Process	Altitude (km) 0	2	6	10
Reactions with Trace gases[a]				
OH	0.75	1.0	1.7	2.8
HO_2	87	100	115	130
Background aerosol	88	107	161	260
Continental aerosol	8.5	41	154	260
Cloud elements		3.5		

[a] Sum of rates given in Tables 1 and 2.

ticle. Accordingly to gas kinetic theory, the rate of collisions per unit volume of molecules present with number density n_1 with aerosol particles in the size range between r and $r+dr$ is

$$\pi(r+r_1)^2(\bar{C}^2+\bar{C}_1^2)^{\frac{1}{2}} n_1 dN \approx r\bar{C}_1 n_1 dN = (\pi/2.3)\bar{C}_1 n_1 r f(r)\,dr \qquad (2)$$

Here, r_1 is the molecular radius and $\bar{C}$ and $\bar{C}_1$ are average velocities of the aerosol particles and the molecules respectively. The simplifications result from the fact that $r \gg r_1$ and $\bar{C}_1 \gg \bar{C}$. In the upper range of aerosol particle sizes the molecular mean free path is small compared with the size of aerosol particles, so that the aerosol in essence represents per unit volume a surface $dA = 4\pi r^2 dN$ for particles in the size range between r and $r+dr$. The rate of collisions of molecules with aerosol particles in this size range according to kinetic theory is

$$(4\pi r^2 dN)(\bar{C}_1 n_1/4) = (\pi/2.3)\bar{C}_1 n_1 r f(r)\,dr \qquad (3)$$

This expression is formally identical with expression (2) derived above for the lower range of size distribution. Hence, it shall be assumed that the same expression is valid also in the transition range. Then the integrated collision rate for the entire distribution of particle sizes is given by

$$\frac{dn_1}{dt} = (\pi/2.3)\bar{C}_1 n_1 \int_0^\infty r f(r)\,dr \qquad (4)$$

To obtain the corresponding reaction rate requires the introduction of an efficiency factor ε in the right hand side of equation (4). For radicals a value of unity will here be assumed for ε, i.e. loss of radicals occurring upon every collision with an aerosol particle. Then the time constant for such loss is

$$\tau = (2.3/\pi\bar{C}_1) \Big/ \int_0^\infty r f(r)\,dr \qquad (5)$$

Table 4 sets out the time constants for the loss of radicals according to eq. (5) as a function of altitude for the two types of aerosol considered. They amount to about 100 sec for loss to background aerosol and about 10 sec for loss to continental aerosol. These time constants are much less than the value of 3×10^3 sec calculated by Levy (1971) using an undisclosed procedure. For comparison, Table 4 shows for the important radicals OH and HO_2 also time constants due to the consumption by gaseous reactions, utilizing the reaction rates listed in Tables 1 and 2. It is evident that the time constant for OH loss by gaseous reactions (less than 1 sec) is too short to be affected much by aerosols. For HO_2 radicals, however, the time constants for loss to aerosol are equal or less than that for gaseous consumption so that in this case the effect of aerosol is significant provided ε is not much different from unity. Loss of HO_2 radicals to aerosols would reduce the rate of formation of OH from HO_2 via the recycling mechanism and would, therefore, lead to a reduction of the steady state OH number densities as required by the observational data.

It should be noted that the above treatment of collisions of radicals with large aerosol particles, representing them as a surface, is correct only if the collision rate is not diffusion-limited. However, since the large aerosol particles make only a small contribution to the overall collision rate involving the total assembly of particle sizes, the error caused by the neglect of diffusion is also small. Moreover, the continuous production of radicals throughout the entire volumen tends to reduce any concentration gradient outside the collision range of the aerosol particle. Compared with the neglect of diffusion, the lack of knowledge concerning the reaction efficiency causes a much greater uncertainty.

Laboratory data on wall destruction effi-

ciencies for HO_2 radicals are scarce, whereas for hydrogen atoms they are abundant (Thrush, 1965). Hoare et al. have estimated that wall destruction of HO_2 is only slightly less efficient than that of H atoms so that surfaces of several metals, graphite and many porous, rough surfaces would provide HO_2 destruction efficiencies in the range of $0.1 < \varepsilon < 1$. Thus, the assumption of unit reaction efficiency in the present case is not entirely unjustified. On the other hand, since the value of ε turns out to be so important it becomes necessary to determine it more quantitatively, preferably by experimental investigation.

Loss of radicals in clouds

For completeness, we present here also time constants for the loss of radicals to cloud elements, the calculation being similar to that for aerosols except for the choice of distribution functions. Two types of clouds were considered (*a*) fair weather cumulus, characterized by a number density of cloud elements of 300 cm^{-3} and a size range of 0–35 μm, (*b*) cumulus congestus, characterized by a number density of cloud elements of 100 cm^{-3} and a size range 0–60 μm. The two size distributions were obtained by composites of the data from Weickmann & aufm Kampe (1953), Durbin (1959), Singleton & Smith (1960). The integrated surface of cloud elements per unit volume was not markedly different in both cases. The derived time constant for radical loss, assuming unit reaction efficiency, is 0.035 sec. Unlike the time constants for collisions with aerosols, a correction for diffusion limitation is required for cloud elements because the size distributions favor particles above 5 μm. For an average droplet size of 10 μm the correction is estimated from the continuum diffusion theory to be about two orders of magnitude, so that the time constant for radical loss increases to 3.5 sec. This value is also entered in Table 4 and refers, of course, to the volume inside the clouds. It indicates that in this environment destruction of both OH and HO_2 radicals by cloud elements competes effectively with loss due to gas phase reactions. Although clouds thus provide sizable sinks for these radicals, they are not very effective for the atmosphere as a whole because they fill only 5 to 10% of the available tropospheric air space. The diffusion of radicals toward clouds can be neglected compared with reactions in the surrounding air.

Conclusions

It has been shown that two sets of observations, the latitudinal distribution of CO mixing ratios and the rate of nitrate precipitation, are inconsistent with the high number densities predicted by Levy (1971, 1973) for OH radicals in the troposphere. It appears that he has underestimated the capability of aerosol particles in scavenging HO_2 radicals. The loss of HO_2 by this or other yet unknown channels would reduce the production of OH radicals due to the reaction of HO_2 with nitric oxide, and thereby lower the steady state OH number density. At present it is still uncertain whether the effect of aerosol scavenging is sufficient to reduce the OH number density by the required amount, and other factors may be more important. The observations indicate that the OH number densities predicted by Levy (1972, 1973) must be reduced by at least a factor of five, probably by a factor of ten. This requirement constitutes mainly a quantitative re-assessment of Levy's model. Qualitatively, the photochemical mechanism proposed by him remains valid.

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О РОЛИ РАДИКАЛОВ ОН И HO_2 В ТРОПОСФЕРЕ

Согласно фотохимической модели, предложенной Леви, эффективная концентрация гидроксильных радикалов в тропосфере имеет порядок $2{,}5 \times 10^6$ молекул/*см*^{3}. Здесь показано, что такие высокие концентрации ОН не согласуются с двумя независимыми наборами наблюдательных данных: распределением отношений смеси CO с широтой в северном и южном полушариях; со скоростью выпадения нитратных осадков в северном полушарии. Верхний предел эффективной концентрации ОН по наблюдениям составляет самое большее 1/5 от предсказанного Леви. Повидимому рекомбинация HO_2 в радикалы ОН не столь эффективна, как предполагается в модели. Представлены вычисления захвата радикалов аэрозольными частицами. Показано, что аэрозольное удаление радикалов ОН пренебрежимо по сравнению с его количеством, идущим на газовые реакции. В то же время аэрозольное удаление радикалов HO_2 могло бы обеспечить их значительный сток.