# A REVIEW ON PERVASIVE ATMOSPHERIC CHEMISTRY OF VOLATILE ORGANIC ACIDS

## Abstract

Emissions of volatile organic acids can cause detrimental impact on the air quality as well as risk to human health and environment. These organic acids are found all through the troposphere at high level concentration in the ppb range. In the forested and rural regions, divergent study reveals strong variations in volatile organic acids concentration, with a considerable decrease from summer to winter. The atmospheric sources of volatile organic acids comprise of mainly emissions from biogenic, anthropogenic and precursors photochemical transformation in the gaseous, particulate and aqueous phases. We also appraise the predominant sources of volatile organic acids, principal sinks of such compounds and their benefaction to tropospheric concentration for various environments. At the tropospheric level, these organic compounds are initiated with the atmospheric oxidants like hydroxyl (OH) radicals, ozone ($O_3$) molecules, nitrate ($NO_3$) radicals, chlorine (Cl) atoms and play a significant role in the lower region of the troposphere. In this review, moreover, the mechanism, kinetics and atmospheric lifetime of the tropospheric reactions of both the biogenic as well as anthropogenic organic acids are bestowed and discussed succinctly.

**Keywords:** VOCs; atmospheric lifetime; reaction mechanism; GWPs.

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## I. INTRODUCTION

### 1. Historical Background

**Haagen-Smit**

In the early 20th century, the purpose and importance of the volatile organic compounds released by human activity were made clear by Haagen-Smit in his ground-breaking study of the Los Angeles smog. He was aware of the critical importance of hydrocarbon oxidation in the presence of sunlight and nitrogen oxides, a photochemical source of ozone and other oxidants. Since then, a comprehensive knowledge of the mechanism of photochemical smog creation has been achieved. Following an understanding of the relevance of biogenic emissions and anthropogenic emissions brought the realization of the organic molecules emitted. Since this early, ground-breaking research, photochemical smog has been discovered in nearly all of the major industrial and urban centers of the world at concentrations that exceed the standards established to safeguard human health [1].

2. **About OVOCs:** Oxygenated volatile organic compounds (OVOCs) released into the atmosphere is likely to contribute the ozone formation and in urban areas the components of photochemical smog are found. The above component formation is initiated through reaction of OVOCs with O3 and Cl atoms as well as OH and NO3 radicals [2]. Production of secondary pollutants such as secondary organic aerosols, peroxy nitrates and ozone in the troposphere get enhance due to OVOCs degradation [3]. On a worldwide basis, hydrocarbons present in the gas phase are the main sources for oxygenated volatile organic compounds (OVOCs). CH4 the simplest hydrocarbon undergoes gas phase oxidation initiated by atmospheric oxidant OH radicals to give HCHO, HC (O) OH, HCHO, and CH3COOH. These above molecules are further oxidized to give CO and CO2. Bulk hydrocarbons oxidation gives rise to diversity of OVOCs [4]. In the gas phase, oxygenated volatile organic compounds undergo chemical and physical process which leads to degradation from the gas phase. OVOCS removal can be through photolysis and by dry and wet deposition. Alkanes have high vapor pressure than the OVOCs. Descending order trend in vapor pressure is alkanes > ethers > aldehydes ~ esters > alcohols > carboxylic acids. For molecules where the carbon number is same there is decrease in vapour pressure as oxygen atoms are added. The transformation of saturated OVOCs may be initiated by the atmospheric oxidant like OH radical, $O_3$ molecule, $NO_3$, Cl atom. Photolysis of ozone form OH radical and their concentration is higher during the day. $NO_3$ radicals undergo rapid photolysis so their concentration is low during the day,

but adequate at night. OVOCs also rapidly react with Cl than other oxidants but this reaction mainly occurs in coastal region [5, 6, and 7].

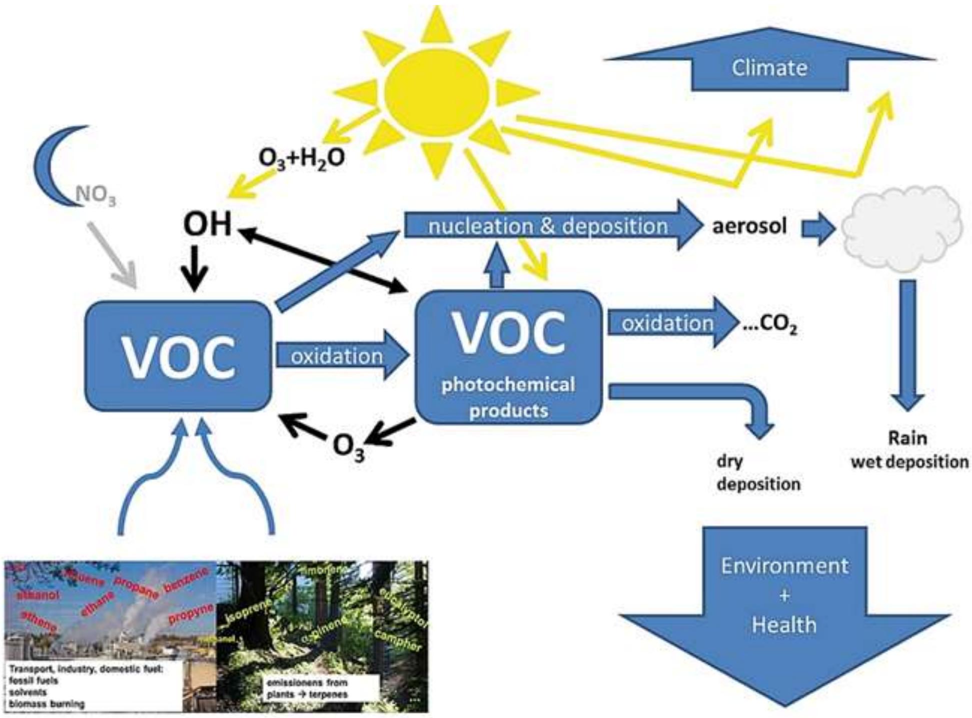

**Figure 1:** Degradation of Volatile Organic Compounds in the Atmosphere. (www.dwd.de/EN/research/observing_atmosphere/composition_atmosphere/trace_gases/cont_nav/voc.html)

A detailed study has been presented upon the volatile organic acids (OVOAs) in this chapter. Organic acids have been paid attention to the last few decades due to their possible effects on climate change and atmospheric heterogeneous chemistry [8]. Atmospheric unsaturated organic acids are responsible for the formation of free acidity in rainwater (in non-urban areas upto 64%). Methacrylic acid and acrylic acid are two exemplars of unsaturated organic acids of which acrylic acid is identified as one of the 189 hazardous air pollutants in the Clean Air Act Amendments by the US Congress [9]. Production of polymers, paper formulation, paper coatings widely use acrylic acid. Emissions of acrylic acid vapors are mainly from factories production of acrylic acid [10]. Naturally acrylic acid is produced in the rumen fluid of sheep and in some species of marine algae [11]. Reaction of unsaturated carboxylic acids and OH radicals occur rapidly. Atmospheric lifetimes for methacrylic acid and acrylic acid are 4 hours and 6 hours respectively. The reaction occurs via addition of OH to the C=C double bond, addition of $O_2$ and NO to give corresponding peroxy radical, which also undergoes scission of C-C bond. Oxidation of methacrylic acid gives pyruvic acid is slow [12]. Carboxylic acids are formed abundantly in atmosphere, soil and aquatic medium [13, 14]. Carboxylic acids degradation mechanism has been focused by only few research groups, inspite of their high reactivity [15].

The photochemical oxidation of succinic acid leads to degradation of succinic acid to malonic acid and then oxalic acid. Due to this oxidation, reduction of the carbonate chain length of succinic acid occurs [16,17]. Cyclopentene and cyclohexene have been indicated as possible anthropogenic precursors of dicarboxylic acid in atmosphere, ranges from C3 – C6. These cycloalkenes are found in automobile exhaust and gasoline [18, 19, and 20].

For instance, the biogenic precursor of azelaic acids and suberic acids are linoleic and oleic acids. The marine origin unsaturated fatty acids are photo-oxidized in the marine atmosphere and as a result a homologues series of carboxylic acids namely malonic, succinic, oxalic and azelaic acid are formed [21]

## II. GLOBAL TROPOSPHERIC DISTRIBUTION AND MIXING RATIOS OF VOAS

The most recent data shows on the prevalence of carboxylic acids, formic acid and acetic acid are common substances in the troposphere. Additionally, metropolitan, continental, and even remote regions of the troposphere have been found to contain higher-molecular-weight carboxylic acids. Carboxylic acids are present in fog, clouds, aerosol particles, rain, snow, ice, and the gas phase [22].

**Table 1: Atmospheric Concentrations of VOAs (Volatile Organic Acids) from Field Measurements**

| Compounds | Level of atmospheric concentrations | Location | References |
|---|---|---|---|
| Formic acid | 13 ppb | Los Angeles | Grosjean 1989 [23] |
| Formic acid | 1.8-14.8 ppbv | Amazonian rain forest | Kawamura et al.1985[24] |
| Formic acid | 1.6±0.6 ppb | Amazonian rain forest | Andreae et al. 1988;[25] |
| Acetic acid | 16 ppb | Amazonian rain forest | Grosjean 1989 [23] |
| Acetic acid | 0.8-5.4 ppbv | Amazonian rain forest | Kawamura et al. 1985[24] |
| Acetic acid | 2.2±1.0 ppb | Amazonian rain forest | Andreae et al. 1988; |
| Propionic | 0.3-0.7 ppbv | Japan rural environment | Satsumabayashi et al. (1989) [26] |
| n-butyric acid | 0.1-0.3ppb | Japan rural environment | Satsumabayashi et al. (1989) [26] |
| Oxalic acid | 690 ng $m^{-3}$ | Hong Kong | Satsumabayashi et al. (1989) [26] |

## III. MAJOR SOURCES OF VOLATILE ORGANIC ACIDS

Carboxylic acids are released from both natural and man-made sources, and they are created in the atmosphere by condensed-phase processes in atmospheric aerosols and ozone-alkene gas-phase interactions [28-32].

1. **Anthropogenic Sources:** “A variety of anthropogenic sources is discussed for carboxylic acids. Among those are animal waste, combustion of synthetic materials, industrial emissions, waste incineration, automobile exhaust and tobacco smoke. These sources are

all significant on a local level, but they don't appear to make much of an impact globally" [33]. Only anthropogenic sources that significantly affect atmospheric carboxylic acid concentrations will be discussed moving forward.

In nonurban environments where intensive biomass burning is now practiced, primary anthropogenic emissions may also be significant. According to Talbot *et al.* [34] and Hartmann [35], the ratio of $CH_3COOH/HCOOH$ emitted by burning biomass ranges from 2 to 10. Talbot *et al.* [34] "established direct emissions of carboxylic acids from biomass combustion represent a source of these acids in the atmosphere. They conducted a burning experiment at a natural location using different fuels (dried wood logs, fresh green vegetation), and they found extremely high concentrations of formic and acetic acid directly above the fire, ranging from 300 to 500 ppbv for formic acid and from 3000 to 5000 ppbv for acetic acid".

Aliphatic organic acids were found in Los Angeles air and a car's motor exhaust when it was idling, according to Kawa Mura *et al.* [36]. Individual acid distribution was similar in air and vehicle exhaust, but exhaust concentrations were 17 times higher. The distribution of these acids was characterized by acetic and formic acids predominating, then propionic acid coming in second. According to their findings, one of the principal sources of organic acids in the air in Los Angeles is automotive exhaust. Later on, an investigation, Dicarboxylic acids detected in gasoline and diesel vehicle exhausts were distributed similarly to urban air samples, according to research by Kawamura et al.[37].

In comparison to the average ambient concentration, the concentrations of these acids in motor vehicle exhausts were 28 (for gasoline) and 144 (for diesel) times greater. The formic and acetic acid emissions from vehicles were also studied by Talbot et al. in 1988[34]. They determined that the motor vehicles are the direct source of the elevated quantities of these acids at the tunnel where approximately $10^5$ cars pass daily.

2. **Biogenic Sources:** Vegetation directly emitting pollutants have been studied more extensively. Formic and acetic acid concentrations in precipitation of continental regions have a seasonal cycle, according to Keene and Galloway [38]. These concentrations are higher in precipitation during the growing season than they are in the winter. These authors propose seasonally variable emissions of carboxylic acids from plants to account for this seasonal change of concentrations. Similar to this, Andreae et al. [39] claimed that direct emission from vegetation is a major source of these acids in the Amazon environment based on their analysis of vertical profiles of tropospheric concentrations of carboxylic acids in the Amazonforest (Brazil). Studies on the actual mechanisms of carboxylic acid emissions from vegetation provided evidence to support this notion. In a study on carboxylic monoacids in the air of the Mayombe Forest (Congo), Servant et al. [40] demonstrated that carboxylic acids, specifically HCOOH, CH3COOH, and CH3CH2COOH, are leached by tree leaves when soaked in deionized water. They calculated the typical fluxes of these acids released directly by various tree species and came to the conclusion that vegetation's direct release of these acids was the primary source of these acids in the boundary layer above the forest. An alternative experiment on the direct emissions of carboxylic acids from tree leaves in the Amazonia jungle (Brazil) was conducted by Talbot et al. in 1990[41]. Every 10 minutes, they took measurements of the formic, acetic, and pyruvic acid concentrations within hermetically sealed plastic bags containing tree branches.

## IV. SOURCES OF THE ATMOSPHERIC OXIDANT

The atmospheric loss processes for the volatile organic acids include reaction with atmospheric oxidants such as the OH radicals, $NO_3$ radical (at nocturnal time), $O_3$ molecule and the Cl atoms [42, 43]. The sources of the atmospheric oxidants are briefly discussed below:

1. **Sources of OH radicals:** In the global atmosphere, the OH radical plays a principal role in scavenging the toxic gases like methane ($CH_4$), $CO_2$, hydrofluorocarbons and volatile organic compounds (VOCs). The significant atmospheric pathways for the OH radical formation are detailed below:

   When the sun's UV light interacts with the $O_3$ ozone in presence of water vapour, OH is formed. Production of OH involves photodissociation of $O_3$ to get $O_2$ or O ($^1$D). Quenching of O ($^1$D) took place by the molecule $N_2$ or $O_2$ forming the initial ground state O ($^3$P). The $O^1D$ atoms are either reacted with water vapour or deactivated to the ground state energy ($O^3P$) [44, 45]

   $$O_3 + h\nu \longrightarrow O_2 + O(^1D) \quad (\lambda \leq 319 \text{ nm}) \qquad (1)$$

   $$O(^1D) + M \longrightarrow O(^3P) + M; \quad (M=O_2, N_2) \qquad (2)$$

   $$O(^1D) + H2O \longrightarrow 2OH \qquad (3)$$

   In urban atmospheric condition, photodissociation of HONO creates the OH radicals. HONO can be produced in the gas phase, in the modest amounts from autos, or via a variety of heterogeneous pathways [46,47,].

   $$HONO + h\nu\ (\lambda \leq 400 \text{ nm}) \longrightarrow OH + NO \qquad (4)$$

   Reaction of NO with hydroperoxy radical ($HO_2$), photolysis of $H_2O_2$, photo-oxidation of acetone and other ketones, alcohols, and aldehydes are some sources for OH formation [48-50].

2. **Sources of $NO_3$ Radicals:** The formation of $NO_3$ radical in the troposphere proceeds via the reaction of NO and $O_3$ molecule. The tropospheric $NO_3$ radical is found to be in low concentration, this is because at daylight hour, the $NO_3$ radicals rapidly react with having the atmospheric lifetime of similar to 5s. But at the nocturnal hour there is measurable increase in in the concentration of $NO_3$ radical. The average nocturnal concentration of the $NO_3$ radical has been proposed to be of $5\times10^{18}$ molecule $cm^{-3}$ for the calculation of lifetime. Also, the measurement of $NO_3$ concentration over the continental areas is found to be of $1\times10^{10}$ molecule $cm^{-3}$. [51-54]

   $$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (5)$$

   $$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad (6)$$

3. **Sources of Cl Atoms:** The most common source of chlorine in the atmosphere is sea salt spray. The main source of Cl atoms in the atmosphere is the reaction of NOX with HCl or NaCl to produce nitryl chloride ($ClNO_2$), which rapidly gets photolyzed to form Cl atoms [55, 56].

$$2NO(g) + NaCl(s) \longrightarrow NaNO_3 + NOCl(g) \quad (7)$$

$$N_2O_5 + NaCl(s) \longrightarrow ClNO_2(s) + NaNO_3(s) \quad (8)$$

$ClNO_2$ was found to accumulate at night and be photolyzed after sunrise to produce chlorine atoms.

Chlorine atoms can be produced by the degradation of organochlorine gases such as $CH_3Cl$, $CH_2Cl2$, $CHCl_3$ and $CH_2ICl$, which are basically of biogenic marine origin with $CH_2Cl_2$ as an exception.

4. **Sources of $O_3$ Molecules:** In the stratospheric layer approximately 90% of $O_3$ molecule is present. “The shielding effect of Ozone layer is responsible for the prevention of harmful ultraviolet (UV) radiations (wavelength ($\lambda$) =100-315 nm) penetrating the earth’s atmospheric layer’’ [57]. $O_3$ regenerates by photo-irradiation of molecular oxygen ($O_2$) with UV rays ($100<\lambda< 240$nm) to form electrically excited free oxygen atom (O ($^3$P)) that reacts with diatomic oxygen ($O_2$) to produce ozone ($O_3$).

$$O_2 + h\nu \ (100 < \lambda < 240 \text{ nm}) \longrightarrow 2\,O(^3P) \quad (9)$$

$$O(^3P) + O_2 \longrightarrow O_3 \quad (10)$$

O3 radical irradiate and decompose back (Eq. (3)) at $\lambda \leq 315$ nm to produce O (3P) and O2. The most of the atmospheric oxygen exists in O2 form [58,59].

$$O_3 + h\nu \ (240 < \lambda < 315 \text{ nm}) \longrightarrow O(^3P) + O_2 \quad (11)$$

## V. REACTION MECHANISM AND KINETICS OF VOAS

Elucidation for the atmospheric reaction of volatile organic compounds and the atmospheric oxidants such as OH radicals, O3 molecules and NO3 radicals have been done over the past decades. The significant reaction mechanism is shown in scheme1.

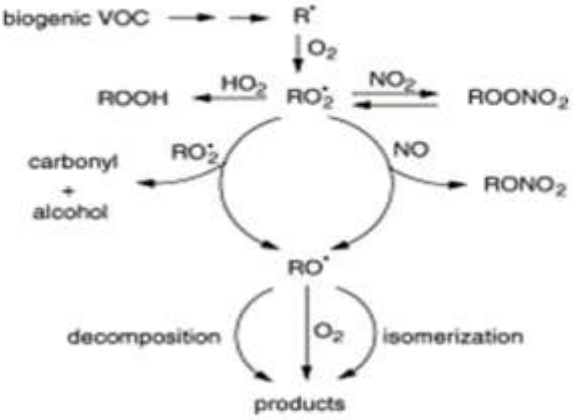

**Figure 2:** Scheme1 for the Addition and H-Abstraction Reaction Mechanism of VOC’s By the Atmospheric Oxidants.

The reaction mechanism generally proceeds via two reaction pathways-

- H-abstraction reaction from C-H bonds
- Addition to C=C bond by OH radicals, $NO_3$ radicals and $O_3$ molecules.

Among the atmospheric oxidants $O_3$ only shows participation in the C=C addition reaction. The OH and $NO_3$ addition reaction is dominant over the H-abstraction reaction, and this leads to the formation of hydroxy or nitro-oxy substituted alkyl radicals respectively [60, 61].

In calculation of rate constant, kinetic model theory is used such as conventional transition state theory (CTST), variational transition state theory (VTST), Rice-Ramsperger-Kassel theory etc. The equation of the kinetic model theory is presented below:

1. **Conventional Transition State Theory (CTST):** Conventional Transition State Theory (CTST) [62] are the keystone for calculation of kinetics in chemical reaction. The CTST is also termed as absolute reaction state it is because the theory assumes a special type of chemical equilibrium (quasi equilibrium) between reactants and activated transition state complexes. The expression for the conventional transition state theory is

$$k = \sigma_r \frac{k_B T}{h} \frac{Q_{TS}}{Q_R \cdot Q_{NO_3}} \exp\left(\frac{-\Delta E}{RT}\right) \qquad (12)$$

   where, $\sigma_r$ is symmetry number, $\tau(T)$ is tunnelling correction factor, $k_B$ is the Boltzmann constant and $h$ is the Planck's constant.

2. **Variational Transition State Theory (VTST):** "Transition state theory is most powerful in the form of variational transition state theory (VTST), especially when combined with modern electronic structure theory, multidimensional tunneling methods, and statistical mechanical and quantum mechanical theory for anharmonicity, and it has become a powerful tool in understanding and predicting chemical reaction mechanisms and reaction rates" [63–73].

$$k^{GT,0}(T,S) = \sigma_r \frac{k_B T}{h} \frac{Q^{GT}(T,S)}{\varphi^R(T)} \exp\left(\frac{-V_{MEP}(S)}{k_B T}\right) \qquad (13)$$

   Where $k_B$ is the Boltzman's constant, $h$ is the Planck's constant, $Q^{GT}$ is generalized partition function, $\varphi^R$ is the partition function of the reactant, $V_{MEP}(S)$ is the value of the potential along the reaction path at $S$.

   - **Acyclic Acids.** The reactivity of acylic acids depends on the length of R alkyl group. Such as the reactivity of acetic acid is faster than that of the formic acid. Formic, acetic, n-propanoic, and n-butanoic acids had lives of 26, 16, 10, and 6 days when reacting with OH radicals, respectively, with a diurnal average [OH] = 1× $10^6$ $cm^{-3}$, correspondingly [74].

   - **Dicarboxylic Acids.** In gas phase dicarboxylic acids are found in small yields in the gas phase and also generated from the oxidation in condensed phase with the species such as glycolaldehyde [$HOCH_2CHO$], glycolic acid [$HOCH_2C(O)OH$] or glyoxal [$HC(O)CHO$]. Further, this multifunctional species gets converted to oxalic acids [75]. “On a timescale of about 1week, heterogeneous processes (rainout and aerosol wet and dry deposition) remove dicarboxylic acids and their condensed-phase derivatives from the atmosphere0” [76].

- **Unsaturated Carboxylic Acids and Keto Acids:** Ozonolysis of diene are the source for the formation of atmospheric unsaturated organic acids. The dominant atmospheric fate of unsaturated carboxylic acids is reaction with OH radicals, which occurs rapid >C=C double bond, the addition of $O_2$ to produce a peroxy radical, and the reaction with NO to produce the matching alkoxy radical, which splits the C-C bond, the reaction takes place. Pyruvic acid [$CH_3C(O)C(O)OH$] is produced by the oxidation of methacrylic acid [$CH_2CCH_3C(O)OH$]. Pyruvic acid [$CH_3C(O)C(O)OH$] has a short half-life of a few hours or less and reacts slowly with OH radicals [75].

## VI. ATMOSPHERIC LIFETIME AND GLOBAL WARMING POTENTIALS

The removal of the atmospheric volatile organic acids occurs through the reaction with atmospheric oxidants such as OH radicals, $NO_3$ radicals, Cl atoms and the $O_3$ molecules. Thus, it can be expressed as [77]

$$\tau_{eff} \approx \tau_x \, [x = OH, O_3, NO_3] \qquad \textbf{(14)}$$

Here, $\tau_{OH} = (k_{OH} \times [OH]^{-1})$, $\tau_{NO3} = (k_{NO3} \times [NO3]^{-1})$ and $\tau_{O3} = (k_{O3} \times [O3]^{-1})$. The global average concentration of OH radicals, $O_3$ molecule and $NO_3$ radicals are estimated to be $1 \times 10^6$ molecule $cm^{-3}$ [78], $5.7 \times 10^8$ molecule $cm^{-3}$ [79] and $7 \times 10^{11}$ [80] molecule $cm^{-3}$ respectively.

Calculation of Global Warming Potential is essential because it gives the measurement on how much heat is trap by the gas in the atmospheric region. We can also measure the radiative forcing efficiency of each gas relative to $CO_2$. The equation given by Hodnebrog *et al.* [81] for calculation of Global Warming Potential is

$$GWP_i\,(H) = \frac{\int_0^H RF_i(t)dt}{\int_0^H RF_{CO_2}(t)dt} = \frac{AGWP_i(H)}{AGWP_{CO_2}} \qquad (15)$$

## VII. CONCLUSION

In this work, we have presented a systematic consequence of the volatile organic acids viz. acylic acids, unsaturated carboxylic acids, keto acids, and dicarboxylic acids. From the last past decades, emissions of volatile organic acids are of major concern. Ground breaking investigations on the global tropospheric volatile organic acids has allowed a better understanding of its distribution (mixing ratios), sources and their loss processes(sink). Anthropogenic emissions and biogenic emissions play an active role for the series of chemical reactions undergone in the tropospheric level. Moreover, atmospheric oxidants (OH, $NO_3$, $O_3$ and Cl) shows dominant chemical sink for the degradation of volatile organic acids. The investigation on atmospheric lifetime renders the stability nature of volatile organic acids as well as the kinetic calculations.

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