

A review on pervasive atmospheric chemistry of volatile organic acids

Moumita Basumatary^a, Shilpa Neog^a, Srutishree Sarma^a, Nand Kishor Gour^{a*} and Ramesh Chandra Deka^{a*}

^aDepartment of Chemical Sciences, Tezpur University, Tezpur-784028, Assam, India

*To whom correspondence should be addressed:

Email: nkgour1@tezu.ernet.in & ramesh@tezu.ernet.in

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 (O₃) molecules, nitrate (NO₃) 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.

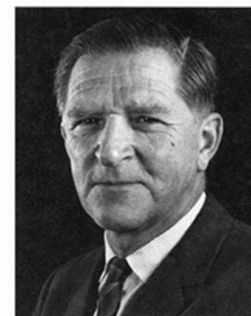


Keywords – VOCs; atmospheric lifetime; reaction mechanism; GWPs

I. Introduction

A. Historical background

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].



Haagen-Smit

B. 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 give 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, O₃ molecule, NO₃, Cl atom. Photolysis of ozone form OH radical and their concentration is higher during the day. NO₃ radicals undergo rapid photolysis so their

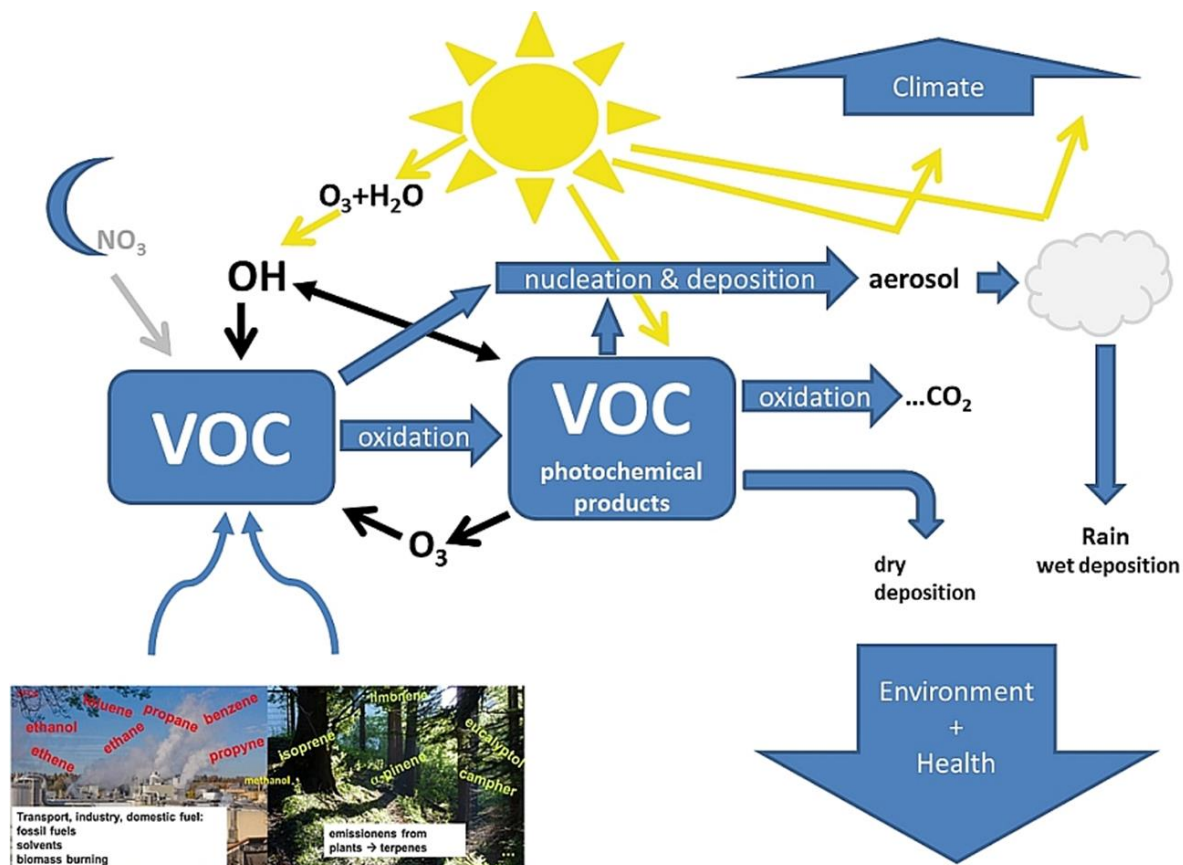


Fig1. Degradation of Volatile organic compounds in the atmosphere.

(www.dwd.de/EN/research/observing_atmosphere/composition_atmosphere/trace_gases/cont_nav/voc.html)

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 [5,6,7].

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 O₂ 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 [18,19,20]. 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].

Table1: 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].

A. 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 CH₃COOH/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 10⁵ cars pass daily.

B. 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.

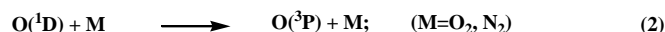
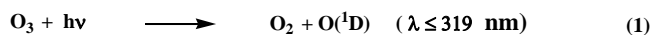
IV. Sources of the atmospheric oxidant

The atmospheric loss processes for the volatile organic acids include reaction with atmospheric oxidants such as the OH radicals, NO₃ radical (at nocturnal time), O₃ molecule and the Cl atoms [42,43]. The sources of the atmospheric oxidants are briefly discussed below:

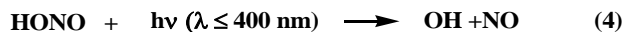
A. Sources of OH radicals

In the global atmosphere, the OH radical plays a principal role in scavenging the toxic gases like methane (CH₄), CO₂, hydrofluorocarbons and volatile organic compounds (VOCs). The significant atmospheric pathways for the OH radical formation are detailed below:

When the sun's UV light interact with the O₃ ozone in presence of water vapour, OH is formed. Production of OH involves photodissociation of O₃ to get O₂ or O(¹D). Quenching of O(¹D) took place by the molecule N₂ or O₂ forming the initial ground state O(³P). The O(¹D) atoms are either reacted with water vapour or deactivated to the ground state energy (O(³P)) [44,45]



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,].



Reaction of NO with hydroperoxy radical (HO₂), photolysis of H₂O₂, photo-oxidation of acetone and other ketones, alcohols, and aldehydes are some sources for OH formation [48-50].

B. Sources of NO₃ radicals:

The formation of NO₃ radical in the troposphere proceeds via the reaction of NO and O₃ molecule. The tropospheric NO₃ radical is found to be in low concentration, this is because at daylight hour, the NO₃ 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 NO₃ radical. The average nocturnal concentration of the NO₃ radical has been proposed to be of 5×10¹⁸ molecule cm⁻³ for the calculation of lifetime. Also, the measurement of NO₃ concentration over the continental areas are found to be of 1×10¹⁰ molecule cm⁻³. [51-54]



C. 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 (ClNO₂), which rapidly gets photolyzed to form Cl atoms [55, 56].

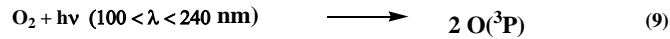


ClNO₂ was found to accumulate at night and be photolyzed after sunrise to produce chlorine atoms.

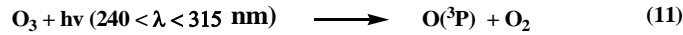
Chlorine atoms can be produced by the degradation of organochlorine gases such as CH₃Cl, CH₂Cl₂, CHCl₃ and CH₂I₂, which are basically of biogenic marine origin with CH₂Cl₂ as an exception.

D. Sources of O₃ molecules:

In the stratospheric layer approximately 90% of O₃ molecule is present. "The shielding effect of Ozone layer is responsible for the prevention of harmful ultraviolet (UV) radiations (wavelength (λ) =100-315 nm) penetrating the earth's atmospheric layer" [57]. O₃ regenerates by photo-irradiation of molecular oxygen (O₂) with UV rays (100<λ< 240nm) to form electrically excited free oxygen atom (O (³P)) that reacts with diatomic oxygen (O₂) to produce ozone (O₃).



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].



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.

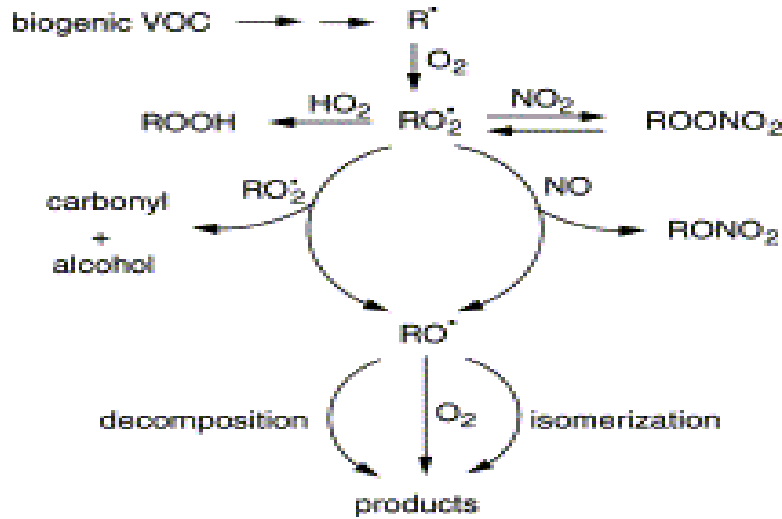


Fig 2. Scheme1 for the addition and H-abstraction reaction mechanism of VOCs by the atmospheric oxidants.

The reaction mechanism generally proceeds via two reaction pathways-

- H-abstraction reaction from C-H bonds
- addition to C=C bond by OH radicals, NO3 radicals and O3 molecules.

Among the atmospheric oxidants O3 only shows participation in the C=C addition reaction. The OH and NO3 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:

A. 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 ---

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

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

B. 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].

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

where k_B is the Boltzman's constant, h is the Planck's constant, Q^{GT} is generalized partition function, φ^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 acyclic 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 $[OH] = 1 \times 10^6 \text{ cm}^{-3}$, 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 1 week, heterogeneous processes (rainout and aerosol wet and dry deposition) remove dicarboxylic acids and their condensed-phase derivatives from the atmosphere" [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]

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

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

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

VII. Conclusion

In this work, we have presented a systematic consequence of the volatile organic acids viz. acyclic 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.

References

1. A.J. Haagen-Smit, "The air pollution problem in Los Angeles," Engineering and Science, vol.14, pp. 7-13, 1955.
2. O.W. Wingenter, M.K. Kubo, N.J. Blake, T.W. Jr Smith, D.R. Blake, and F.S. Rowland, "Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights," Journal of Geophysical Research: Atmospheres, vol.101, pp. 4331-4340, 1996.
3. R.G. Derwent, M.E. Jenkin, and S.M. Saunders, "Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions," Atmospheric Environment, vol. 30, pp. 181-199, 1996.
4. J. Calvert, A. Mellouki, and J. Orlando, Mechanisms of atmospheric oxidation of the oxygenates, 2011.
5. A. Mellouki, G. Le Bras, and H. Sidebottom, "Kinetics and mechanisms of the oxidation of oxygenated organic compounds in the gas phase," Chemical reviews, vol. 103 pp. 5077-5096, 2003.
6. P. Lin, J.Z. Yu, G. Engling, and M. Kalberer, "Organosulfates in humic-like substance fraction isolated from aerosols at seven locations in East Asia: A study by ultra-high-resolution mass spectrometry," Environmental science & technology, vol. 46 pp. 13118-13127, 2012.
7. M. Glasius, M. Lahaniati, A. Calogirou, D.Di Bella, N. R. Jensen, J. Hjorth, and B. R. Larsen, "Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone," Environmental Science & Technology, vol.34, pp. 1001-1010, 2000.
8. H.B. Singh, and J.F. Kasting, "Chlorine-hydrocarbon photochemistry in the marine troposphere and lower stratosphere. Journal of atmospheric chemistry," vol.7, pp. 261-285, 1988.
9. A. Mellouki, T.J. Wallington, and J. Chen, "Atmospheric chemistry of oxygenated volatile organic compounds: impacts on air quality and climate," Chemical reviews, vol.115 pp. 3984- 4014, 2015.
10. P. Khare, N. Kumar, K.M. Kumari, and S.S. Srivastava, "Atmospheric formic and acetic acids: An overview," Reviews of Geophysics, vol.37 pp. 227-248, 1999.
11. W.C Keene, and J.N. Galloway, "Considerations Regarding Sources for Formic and Acetic Acids in the Troposphere," Journal of Geophysical Research: Atmosphere, vol. 91 pp. 14466-14474, 1986.
12. T.E. Graedel, Chemical Compounds in the Atmosphere. Academic Press, New York, 1978 pp.217- 218,
13. P. H. Howard, Handbook of Environmental Fate and Exposure Data for Organic Chemical, 1993 pp.71-75,
14. N.K.V. Leitner, and M. Dore, "Hydroxyl radical induced decomposition of aliphatic acids in oxygenated and deoxygenated aqueous solutions," Journal of Photochemistry and Photobiology A: Chemistry, vol. 99 pp.137-143, 1996.
15. B. Ervens, G. Feingold, G.J. Frost, and S.M. Kreidenweis, "A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production," Journal of Geophysical Research: Atmospheres, vol.109, 2004.
16. H. Herrmann, D. Hoffmann, T. Schaefer, P. Bräuer, and A. Tilgner, "Tropospheric aqueous phase free-radical chemistry: Radical sources, spectra, reaction kinetics and prediction tools," Chemical Physics Chemistry, vol. 11 pp. 3796-3822, 2010.

17. D. Schuetzle, D. Cronn, A. L. Crittenden, and R.J. Charlson, "Molecular composition of secondary aerosol and its possible origin. *Environmental Science & Technology*," vol. 9 pp. 838- 845, 1975.
18. D. Grosjean, K. Van Cauwenberghe, J.P. Schmid, P.E. Kelley, and J.N. Jr Pitts, "Identification of C3-C10 aliphatic dicarboxylic acids in airborne particulate matter," *Environmental Science & Technology*, vol. 12 pp. 313-317,1978.
19. K. Kawamura, and K. Ikushima, "Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere," *Environmental Science & Technology*, vol. 27 pp. 2227-2235, 1993.
20. R. Atkinson, D.L. Baulch, R.A. Cox, R.F.Jr Hampson, J.A. Kerr, M.J. Rossi, and J. Troe, "Evaluated kinetic and photochemical data for atmospheric chemistry, organic species: Supplement VII," *Journal of Physical and chemical reference Data*, vol. 28 pp. 191-393, 1999.
21. K. Kawamura, R. Seméré, Y. Imai, Y. Fujii, and M. Hayashi, "Water soluble dicarboxylic acids and related compounds in Antarctic aerosols," *Journal of Geophysical Research: Atmospheres*, vol.101, pp. 8721-18728, 1996.
22. A. Chebbi, and P. Carlier, "Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review," *Atmospheric Environment*, vol. 30, pp. 4233-49, 1996.
23. D. Grosjean, "Organic acids in southern California Air: Ambient concentrations, mobile source emissions, in situ formation and removal processes," *Environmental Science and Technology*, vol. 23, pp. 1506-14, 1989.
24. K. Kawamura, L.L. Ng, and I.R. Kapan, "Determination of organic acids (C1—C10) in the atmosphere, motor exhausts, and engine oils," *Environmental Science and Technology*, vol.19, pp. 1082-6, 1985.
25. M.O. Andreae, R.W. Talbot, T.W. Andreae, and R.C. Harriss, "Formic and acetic acid over the central Amazon region, Brazil 1. Dry seaso," *Journal of Geophysical Research*, vol. 93 pp. 1616-24, 1988.
26. H. Satsumabayashi, H. Kurita, Y. Yokouchi, and H. Ueda, "Mono-and di-carboxylic acids under long-range transport of air pollution in central Japan," *Tellus b: Chemical and Physical Meteorology*, vol.41, pp. 219-229, 1989.
27. K.F. Ho, S.C. Lee, J.J. Cao, K. Kawamura, T. Watanabe, Y. Cheng, and J.C. Chow, "Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong," *Atmospheric Environment*, vol. 40 pp. 3030-3040, 2006.
28. M. Glasius, M. Lahaniati, A. Calogirou, D. Di Bella, N.R. Jensen, J. Hjorth, D. Kotzias, B.R. Larsen, "Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone," *Environmental Science & Technology*, vol. 34 pp. 1001-1010, 2000.
29. G.E. Orzechowska, H.T. Nguyen, S.E. Paulson, "Photochemical Sources of Organic Acids. 2. Formation of C5- C9 Carboxylic Acids from Alkene Ozonolysis under Dry and Humid Conditions," *The Journal of Physical Chemistry A*, vol. 109, pp. 5366-5375. 2005,
30. G.E. Orzechowska, and S.E. Paulson, "Photochemical sources of organic acids. 1. Reaction of ozone with isoprene, propene, and 2-butenes under dry and humid conditions using SPME," *The Journal of Physical Chemistry A*, vol.109, pp. 5358-5365. 2005,
31. A.A. Presto, K.E.H. Hartz, and N.M. Donahue. Secondary organic aerosol production from terpene ozonolysis. 1. Effect of UV radiation," *Environmental science & technology*, vol.39, pp. 7036-7045, 2005
32. B. Ervens, G. Feingold, G. J. Frost, S. M. Kreidenweis, *Journal of Geophysical Research: Atmosphere*, vol. 109, 2004.
33. T.E. Graedel, D.T. Hawkins and L.D. Claxton Carboxylic acids. In *Atmospheric Chemical Compounds: Occurrence and Bioassay*, pp. 342-357. Academic, Orlando, FL.
34. R.W. Talbot, K.M. Beeche, R.C Harris and W. R. Corer III, "Atmospheric geochemistry of formic and acetic acids at a midlatitude temperate site," *Journal of Geophysical Research: Atmospheres*, vol. 93, pp. 1638-1652,1988
35. W. R Hartmann, Carboxylic acids in the atmosphere. Ph.D. thesis, Johannes Gutenberg Universitat, Mainz (German), 1990.
36. K. Kawamura and I. R. Kaplan, "Determination of organic acids (CrC10) in the atmosphere, motor exhausts, and engine oils," *Environmental Science and Technology*, vol.19, pp.1082-1086, 1985.
37. K. Kawamura and I.R. Kaplan, "Motor exhaust emissions as primary source for dicarboxylic acids in Los Angeles ambient air," *Environmental Science & Technology*, vol. 21, pp. 105-110, 1987.
38. W.C. Keene and J.N. Galloway, "The biogeochemical cycling of formic and acetic acids through the troposphere: an overview of current understanding," *Tellus B*, vol. 40 pp. 322-334, 1988.
39. M.O. Andreae, R.W. Talbot, T.W. Andreae and R.C. Harris, "Formic and acetic acid over the central Amazon region, Brazil. 1. Dry season," *Journal of Geophysical Research*. vol. 93, pp. 1616-1624, 1988.
40. J. Servant, G. Kouadio, B. Cros and R. Delmas, "Carboxylic monoacids in the air of Mayombe forest (Congo): role of the forest as source or sink. *Journal Atmospheric Chemistry*," vol. 12, 367-380, 1991.
41. R. W. Talbot, M. O. Andreae, H. Berressein, D.J. Jacob and K.M. Beecher, "Sources and sinks of formic, acetic, and pyruvic acids over central Amazonia. 2." Wet season. *Journal of Geophysical Research*, vol. 881, pp. 799-16, 1990.
42. R. Atkinson, 2000. Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment* 34, 2063-2101.
43. K.W. Oum, M.J. Lakin, D.O. Dehaan, T. Brauers, and B.J. Finlayson-Pitts, "Formation of molecular chlorine from the photolysis of ozone and aqueous sea-salt particle," *Science*, vol. 279, pp.74-77, 1998.
44. J. Lelieveld, et al., "Atmospheric oxidation capacity sustained by a tropical forest," *Nature* vol. 452, pp. 737-740, 2008.
45. S. A. Montzka, et al., "Small interannual variability of global atmospheric hydroxyl," *Science* vol. 331, 67-69 (2011).
46. D.R. Crosley, "The measurement of OH and HO2 in the atmosphere, *Journal of Atmospheric Science*," vol. 52, pp.3299-3314, 1995.
47. S. Madronich and C. Granier, "Impact of Recent Total Ozone Changes on Tropospheric ozone photodissociation, hydroxyl radicals and methane trends," *Geophysical Research Letters*, vol. 19, pp.465-467, 1992.
48. G. Villena, P. Wiesen, C.A. Cantrell, F. Flocke, A. Fried, S.R. Hall, R.S. Hornbrook, D. Knapp, E. Kosciuch, R.L. Mauldin, J.A. McGrath, D. Montzka, D. Richter, K. Ullmann, J. Walega, P. Weibring, A. Weinheimer, R.M. Staebler, J. Liao, L.G. Huey, and J. Kleffmann, "Nitrous acid (HONO) during polar spring in Barrow, Alaska: A net source of OH radicals?," *Journal Geophysical Research Atmosphere*, vol.116 pp.1-12, 2011.
49. Y. Elshorbany, I. Barnes, K.H. Becker, J. Kleffmann, and P. Wiesen, "Sources and cycling of tropospheric hydroxyl radicals - An overview," *Zeitschrift für Physikalische Chemie*, vol. 224 pp. 967-987, 2010
50. B.H. Czader, B. Rappenglück, P. Percell, D.W. Byun, F. Ngan, and S. Kim, "Modeling nitrous acid and its impact on ozone and hydroxyl radical during the Texas Air Quality Study 2006," *Atmospheric Chemistry and Physics*, vol.12 (2012) 6939-6951.
51. D. Stone, L.K. Whalley, D.E. Heard, Tropospheric OH and HO2 radicals: Field measurements and model comparisons, *Chem. Soc. Rev.* 41 (2012) 6348-6404.
52. R. Atkinson, A.M. Winer, J.N. Jr. Pitts Estimation of night-time N2O5 concentrations from ambient NO2 and NO3 radical concentrations and the role of N2O5 in night time chemistry. *Atmospheric Environment* 20, 331-339. 1986.
53. D. Mihelcic, D. Klemp, P. Musgen, H.W. Patz, and Thomas. A. Volz-, "Simultaneous measurements of peroxy and nitrate radicals at Schauinsland," *Journal of Atmospheric Chemistry*, vol. 16, pp. 313-335, 1993
54. U., Platt, F., Heintz, "Nitrate radicals in tropospheric chemistry," *Israel Journal of Chemistry*, vol. 34, pp. 289-300, 1994.
55. R. Atkinson, Kinetics and mechanisms of the gas-phase reactions of the NO3 radical with organic compounds. *Journal of Physical and Chemical Reference Data* 20, pp. 459-507, 1991.
56. T.P. Riedel, T.H. Bertram, T.A. Crisp, E.J. Williams, B.M. Lerner, A. Vlasenko, S.M. Li, J. Gilman, J.de Gouw, D.M. Bon, N.L. Wagner, S.S. Brown, and J.A. Thornton, "Nitryl Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer," *Environmental Science & Technology*, vol.46, pp. 10463-10470, 2012.
57. B.J. Finlayson-Pitts, M.J. Ezell, and J.N. Pitts, "Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N2O5 and ClONO2," *Nature*, vol. 337, pp. 241-244, 1989
58. K.L. Gleason, Stratospheric Ozone: Monitoring and Research in NOAA 2008. <http://www.ozonelayer.noaa.gov/index.htm>
59. J. K. Angell, J. Korshover, J. Quasi-biennial and long-term fluctuations in total ozone. *Monthly Weather Review*, vol. 101, pp. 426-443, 2005.
60. R. Atkinson, "Atmospheric reactions of alkoxy and β - hydroxyalkoxy radicals," *International Journal of Chemical Kinetics*, vol. 29 pp. 99-111, 1997.
61. R. Atkinson, "Atmospheric chemistry of VOCs and NOx," *Atmospheric Environment*, vol. 34, pp. 2063-2101, 2000.
62. K.J. Laidler, *Chemical Kinetics*, 3rd ed., Pearson Education , Delhi, 2004.

63. D.G. Truhlar, W. L. Hase, and J. T. Hynes, "Current status of transition-state theory," *The Journal of Physical Chemistry*, vol. 87, pp.2664-2682, 1983.
64. D.G. Truhlar, D.H. Lu, S. C. Tucker, X. G. Zhao, A. Gonzalez-Lafont, T. N. Truong, and G.C. Lynch. Variational Transition-State Theory with Multidimensional, Semiclassical, Ground-State Transmission Coefficients: Applications to Secondary Deuterium Kinetic Isotope Effects in Reactions Involving Methane and Chloromethane, 1992.
65. D.G. Truhlar, B.C. Garrett, and S.J. Klippenstein, "Current status of transition-state theory," *The Journal of physical chemistry*, vol.100, 12771-12800, 1996.
66. M. B. Hall, P. Margl, G. Na'ray-Szabo', V. L. Schramm, D. G. Truhlar, R. A. van Santen, A. Warshel and J. L. Whitten, *ACS Symp. Ser.*, 1992, 721, 2.
67. J. Gao, and D.G Truhlar, "Quantum mechanical methods for enzyme kinetics," *Annual Review of Physical Chemistry*, vol. 53, pp.467-505, 2002.
68. D.G. Truhlar, J. Gao, M. Garcia-Viloca, C. Alhambra, J. Corchado, M. Luz Sanchez, and T.D. Poulsen, Ensemble-averaged variational transition state theory with optimized multidimensional tunneling for enzyme kinetics and other condensed-phase reactions. *International journal of quantum chemistry*, vol. 100, pp. 1136-1152, 2004.
69. M. Garcia-Viloca, J. Gao, M. Karplus, and D.G. Truhlar, "How enzymes work: analysis by modern rate theory and computer simulations," *Science*, vol. 303, pp.186-195, 2004.
70. G. Truhlar, "Variational transition-state theory and multidimensional tunneling for simple and complex reactions in the gas phase, solids, liquids, and enzymes," In *Isotope effects in chemistry and biology*, pp. 579-619. CRC Press. (2005).
71. J.A. Fernández-Ramos Miller, S.J. Klippenstein, and D.G. Truhlar, "Modeling the kinetics of bimolecular reactions.," *Chemical reviews*, vol. 106, pp.4518-4584, 2006.
72. A. Dybala-Defratyka, P. Paneth and D.G. Truhlar, Quantum Catalysis in Enzymes, in *Quantum Tunneling in Enzyme Catalyzed Reactions*, ed. R. K. Allemann and N. S. Scrutton, RSC Publishing, Cambridge, UK, pp. 36, 2009
73. B. Ervens, G. Feingold, G.J. Frost, and S.M. Kreidenweis, *Journal of Geophysical Research: Atmosphere*. 2004, 109, D15208.
74. J. G. Calvert, A. Mellouki, J.J. Orlando, M.J. Pilling, and T.J. Wallington, *The Mechanisms of Atmospheric Oxidation of the Oxygenates*; Oxford University Press: New York, 2011.
75. G.E. Orzechowska, and S.E. Paulson, "Photochemical sources of organic acids. 1. Reaction of ozone with isoprene, propene, and 2-butenes under dry and humid conditions using SPME," *The Journal of Physical Chemistry A*, vol. 109, pp. 5358, 2005.
76. A. Mellouki, and Y.J. Mu, "On the atmospheric degradation of pyruvic acid in the gas phase. *Journal of Photochemistry and Photobiology A: Chemistry*," vol. 157, pp. 295-300, 2003.
77. V.C. Papadimitriou, K.G. Kambanis, Y.G. Lazarou, and P. Papagiannakopoulos, "Kinetic study for the reactions of several hydrofluoroethers with chlorine atoms," *Journal of Physical Chemistry*, vol. 108, pp.2666-2674, 2004.
78. R.G. Prinn, J. Huang, R.F. Weiss, D.M. Cunnold, P.J. Fraser, P.G. Simmonds, A. McCulloch, C. Harth, P. Salameh, S. O'doherty, and R.H. Wang, "Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades," *Science*, vol. 292, pp. 1882-1888, 2001.
79. J.A Logan, "Tropospheric ozone: seasonal behavior, trends, and anthropogenic influence." *Journal of Geophysical Research Atmosphere*, vol. 90 pp.10463-10482, 1985.
80. R Atkinson, " Kinetics and mechanisms of the gas phase reactions of the NO₃ radical with organic compounds." *J Phys Chem Ref Data* 20, pp.459-50, 1991.
81. Ø, Hodnebrog, M. Etminan, J.S, Fuglestedt, G. Marston, G. Myhre, C.J. Nielsen, K.P. Shine, and T.J Wallington Global warming potentials and radiative efficiencies of halocarbons and related compounds: a comprehensive review. *Rev Geophys* 51:300-3, 2013.