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The Chemistry of Dicarboxylic Acids in the Atmospheric Aerosols

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Additional information is available at the end of the chapter

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1. Introduction

Atmospheric chemistry is a branch of atmospheric science in which the chemistry of the Earth's atmosphere and that of other planets is studied. It is a multidisciplinary field of research and draws on environmental chemistry, physics, meteorology, computer modeling, oceanography, geology and volcanology and other disciplines. It also deals with chemical compounds in the atmosphere, their distribution, origin, chemical transformation into other compounds and finally their removal from the atmospheric domain. These substances may occur as gasses, liquids or solid. The composition of the atmosphere is dominated by the gasses nitrogen and oxygen in proportions that have been found to be invariable in time and space at altitudes up to 100 km. All other compounds are minor ones, with many of them occurring only in traces.

The composition and chemistry of the atmosphere is of importance for several reasons, but primarily because of the interactions between the atmosphere and living organisms. The composition of the Earth's atmosphere (Figure 1) has been changed by human activity and some of these changes are harmful to human health, crops and ecosystems. Examples of problems which have been addressed by atmospheric chemistry include acid rain, photochemical smog and global warming. Atmospheric chemistry seeks to understand the causes of these problems, and by obtaining a theoretical understanding of them, allow possible solutions to be tested and the effects of changes in government policy evaluated.

Observations, lab measurements and modeling are the three important methodologies in atmospheric chemistry. Progress in atmospheric chemistry is often driven by the interactions between these components and they form an integrated whole. For example observations may tell us that more of a chemical compound exists than previously thought possible. This will stimulate new modelling and laboratory studies which will increase our scientific understanding to a point where the observations can be explained. Measurements

made in the laboratory are essential to our understanding of the sources and sinks of pollutants and naturally occurring compounds. Lab studies tell us which gases react with each other and how fast they react. Measurements of interest include reactions in the gas phase, on surfaces and in water. Also of high importance is photochemistry which quantifies how quickly molecules are split apart by sunlight and what the products are plus thermodynamic data such as Henry's law coefficients.

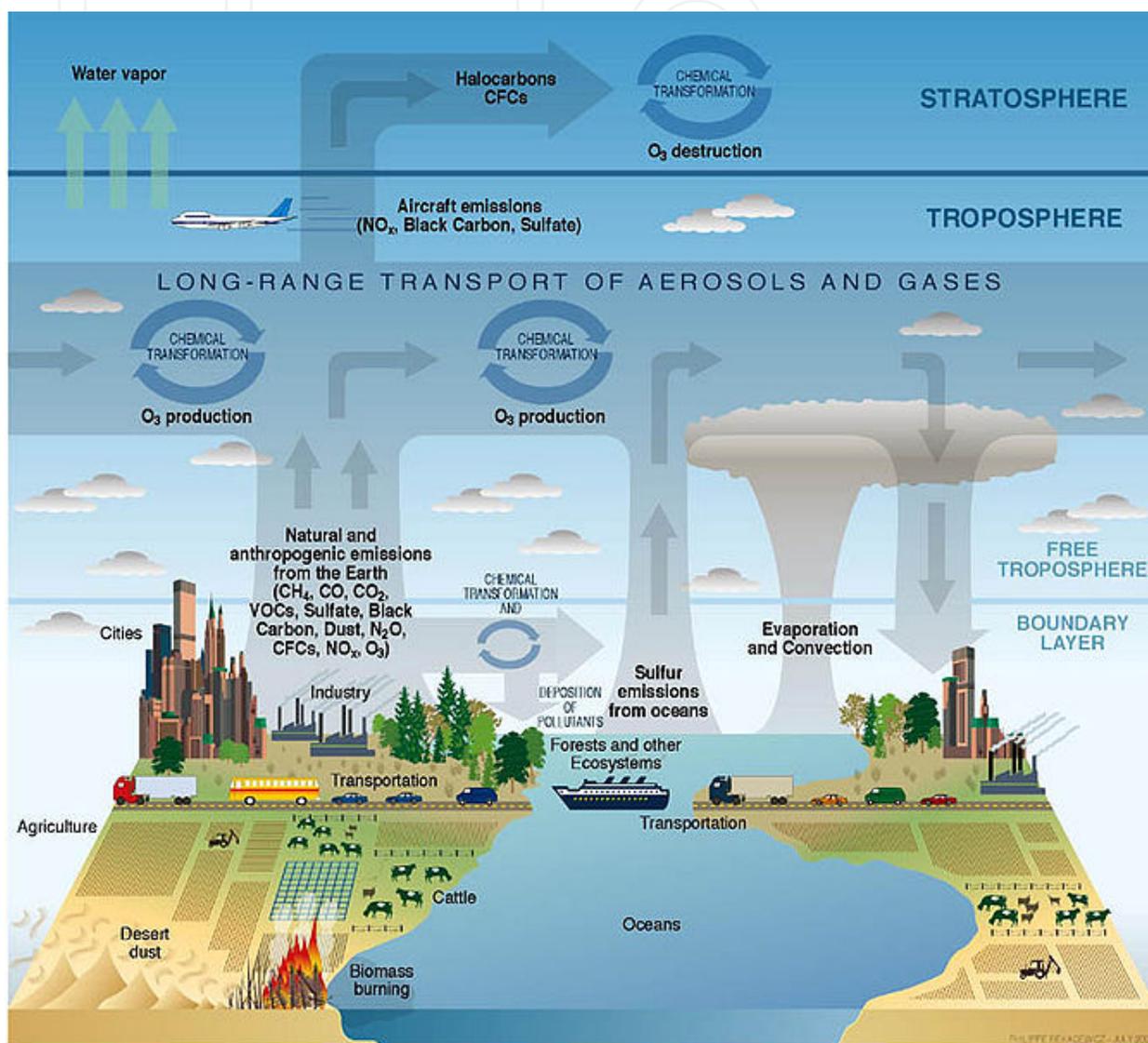


Figure 1. Schematic of chemical and transport processes related to atmospheric composition.

Modelling for instance is important to synthesize and test theoretical understanding of atmospheric chemistry. Computer models (such as chemical transport models) are used. Numerical models solve the differential equations governing the concentrations of chemicals in the atmosphere. They can be very simple or very complicated. One common trade off in numerical models is between the number of chemical compounds and chemical reactions modelled versus the representation of transport and mixing in the atmosphere. For example, a box model might include hundreds or even thousands of chemical reactions but

will only have a very crude representation of mixing in the atmosphere. In contrast, 3D models represent many of the physical processes of the atmosphere but due to constraints on computer resources will have far fewer chemical reactions and compounds. Models can be used to interpret observations, test understanding of chemical reactions and predict future concentrations of chemical compounds in the atmosphere. One important current trend is for atmospheric chemistry modules to become one part of earth system models in which the links between climate, atmospheric composition and the biosphere can be studied.

2. Background knowledge

2.1. Aerosol

An aerosol is a system (in the sense of a system as used in thermodynamics or chemistry) comprising liquid and/or solid particles in a carrier gas. It is generally defined as a suspension of liquid or solid particles in a gas, with particle diameters in the range of 10^{-9} - 10^{-4} m (lower limit: molecules and molecular clusters: upper limit: rapid sedimentation). The most evident examples of aerosols in the atmosphere are clouds, which consist primarily of condensed water. The suspension of the particles in the gas must be significantly stable and homogenous. Hence the assumptions of stability and homogeneity, and consequently the possibilities to use statistical descriptors, are limited to understand and to predict the system, the particle properties, i.e. their size, shapes, chemical compositions, their surfaces, their optical properties, their volumes and masses must be known (Preining, 1993). Aerosol particles scatter and absorb solar and terrestrial's radiation, they are involved in the formation of clouds and precipitation as cloud condensation and ice nuclei, and they affect the abundance and distribution of atmospheric traces gases by heterogeneous chemical reactions and other multiphase processes.

2.2. Aerosol types

The atmospheric aerosol in the boundary layer and the lower troposphere is different for different regions, the main types are:

- a. continental aerosol - a main component of which is mineral dust;
- b. maritime aerosol - a main component of which is sea salt;
- c. background aerosol - aged accumulation mode aerosol.

Chemically or photochemically produced from precursor gases, continental or oceanic biosphere or from anthropogenic releases including sulphates, nitrates, hydrocarbons, soot and so on. The continental aerosols are strongly influenced by man's activities and include urban and rural aerosols. Dust storms produce another type of continental aerosol. Aerosols with a lifetime of up to several years exist in the stratosphere, the sources of which are volcanic injections, and particles or gases entering the stratosphere via diffusion from the troposphere as well as interplanetary dust entering from space. The most important source

is volcanic injection. Due to their long lifetime, these aerosols are distributed relatively homogeneously throughout the whole stratosphere and the size distribution is unimodal with only the accumulation mode present.

2.3. The study of atmospheric aerosols

Atmospheric aerosol particles are a ubiquitous part of earth's atmosphere, present in very lungful of air breathed. They are produced in vast numbers by both human activity (anthropogenic) and natural sources and subsequently modified by a multitude processes. They are known to be crucially important in many issues that directly affect everyday life which include respiratory health, visibility, clouds, rainfall, atmospheric chemistry and global regional climate but they are also one of the more poorly understood aspects of the atmosphere. These shortcomings in understanding are partly due to their small size, which is typically of the order of microns or less, making them difficult to study and also the fact that the processes involved are complex. The description of the organic chemistry in atmospheric aerosol is by no means straightforward, but the addition of the solubility variables, aerosol thermodynamic, hygroscopic properties, deliquescence behaviour makes understanding the atmosphere and its effect is even more challenging, requiring the application of wide spectrum of scientific disciplines including chemistry, physics, mechanics, biology and medicine.

2.4. Aerosols and effect on quality of life

The effects of aerosols on the atmosphere, climate and public health are among the central topics in current environmental research. Urban areas have always been known to be a major source of particulate pollution (Finlayson-Pitts, 2000) which is expected to continue to increase due to world population growth and increasing industrialization and energy use, especially in developing countries (Fenger, 1999). The most obvious effects are the contributions to unsightly smogs and visible deterioration of the building materials (Grossi, 2002). In addition, the fact that urban particulate pollution impact directly on human health has been known for centuries (Brimblecombe, 1987) and has been the subject of much research (Adam et al., 1999).

In an attempt to reduce the health burden of atmospheric particulate pollution, regulatory authorities have attempted to place controls on the emission and the magnitude of pollution episodes within conurbations. The monitoring of particulate air pollution has traditionally focused on particles of less than 10 μm in aerodynamic diameter (the PM_{10} standard), as these are more likely to pass the throat when inhaled (DEFRA, 2005; Larrsen, 1999) but it has become apparent that the smaller particles are more significant, as these particles will penetrate deeper into the lungs and potentially cause more physiological distress or damage. This has led to the use of the $\text{PM}_{2.5}$ standard in countries such Malaysia, where the total mass of particulate matter less than 2.5 μm in diameter is monitored (MOSTI, 2000).

2.5. Composition of atmospheric aerosol

The atmospheric aerosol consists of a complex mixture of organic and inorganic compounds (Cruz, 1998). The typical composition of fine continental aerosol will usually contain various sulphates (mostly ammonium and calcium), nitrates (mostly ammonium), chlorides (mostly sodium), elemental carbon (EC) and organic carbon (OC), especially traffic-related soot, biological materials and other organic compounds, iron compounds, trace metals, and mineral derived from rocks, soil and various human activities. Aerosol composition also can be influenced by local geology, geographic location and climate (Moreno et al., 2003).

2.5.1. Organic and elemental carbon of aerosol

Several studies have shown that over 30% of aerosol is organic carbon, and carbon containing matter can account for as much as 50%. Typically, two classes of carbonaceous aerosol are commonly present in ambient air: organic carbon (OC) and elemental carbon (EC), which are the largest contributors to the fine particle burden in urban atmospheres and heavily industrialised areas (Cachier et al., 1989).

Field measurements also shown a significant mass fraction of atmospheric aerosol consist of organic compounds (Rogge et al., 1991). Around 5 to 10% of the known fraction is often limited to low molecular weight species, which are identified by standard analytical techniques, using gas chromatography coupled with mass spectrometry. A significant fraction of the organic mass in tropospheric aerosol, is comprised of high molecular weight, oxygenated species which remain unidentified (Decesari et al., 2002).

Organic compounds are emitted into the atmosphere from various anthropogenic and biogenic sources. These include primary emission, mainly from combustion and biogenic sources and secondary organic aerosol resulting from the reaction of primary volatile organic compounds in the atmosphere (Fisseha et al., 2004). In urban areas, a number of emission sources are responsible for the presence of organic aerosol in the atmosphere among which are road traffic, industrial processes, waste incineration, wastewater treatment processes and domestic heating. Some of these are pure organic aerosols, which may be formed by primary particle emissions (primary organic carbon) or produced from atmospheric reactions involving gaseous organic precursors (secondary OC) (Cruz and Pandis, 1998).

Organic material is important in controlling the aerosol physico-chemical properties (Cornell et al., 2003). They also found that the uptake of liquid water in aerosol was enhanced by the presence of organic carbon compounds. Organic carbon is also an effective light scatter and may contribute significantly to both visibility degradation and direct aerosol climate forcing (Heintzenberg, 1989). Elemental carbon (often named black carbon or soot) may be the second most important elemental in global warming in terms of direct forcing, after CO₂ due to specific surface properties. Elemental carbon provides a good adsorption site for many semi-volatile compounds such as poly-aromatic hydrocarbon (PAH) and offers a large specific surface area for interactions with reactive trace gases such as ozone. Annually, about 13 Tg black carbons are emitted into the atmosphere, mainly through fossil fuel combustion and biomass burning (Jacob, 1999).

As for other aerosols, the removal of particulate carbon is likely to occur via two main scavenging processes: the in-cloud process, whereby particles are directly incorporated into cloud droplets; and the below-cloud process, where particles are washed out by precipitation itself. The physico-chemical atmospheric processes which transform young combustion particles, expected to be hydrophobic, into a water soluble aerosol phase remains a major unknown. The atmospheric behaviour of the carbonaceous particles is likely to be dictated by the chemical nature of their surfaces (Cachier et al., 1989). If the surface is hydrophobic, the particle remains inactive. However, if it is coated with hygroscopic substances, it may be activated enough to be incorporated into water droplets (Charlson and Heintzenberg, 1995).

2.5.2. Water soluble organic compounds

A significant fraction of the particulate organic carbon is water soluble, ranging from 20% to 70% of the total soluble mass, thus making it important to various aerosol-cloud interactions (Decesari et al., 2000; Facchini et al., 2000). Water soluble organic compounds (WSOC) contribute to the ability of the particles to act as cloud condensation nuclei (CCN) (Novokov and Penner, 1993).

WSOC have been postulated to be partially responsible for the water uptake of airborne particulate matter, which can substantially affect the physical and chemical properties of atmospheric aerosols (Yu et al., 2005). Decesari et al. (2001) have suggested that WSOC are composed of highly oxidised species with residual aromatic nuclei and aliphatic chains. The current understanding of atmospheric particles describes their WSOC fraction as a complex mixture of very soluble organic compounds, slightly soluble organic compounds, and some undetermined macromolecular compounds (MMCs) (Saxena and Hildemann, 1996).

The composition of WSOC varies among sampling regions. It was found to constitute between 20 and 67% of the total organic carbon present in aerosol samples collected in Tokyo (Sempere and Kawamura, 1994). The percentage is ranged from 65 to 75% in aerosol samples collected in Hungary, Italy and Sweden (Zappoli et al., 1999). The study also found that the percentage of WSOC species with respect to the total soluble mass was much higher at the background site (Aspvreten, Central Sweden) (c.a. 50%) compared to the polluted site (San Pietro Copofiume, Po Valley, Italy) (c.a. 25%). A very high fraction (over 70%) of organic compounds in the aerosol consisted of polar species. A study by Wang et al. (2002) showed that most water soluble carbon is total organic carbon (TOC) and range between 20.53 to 35.58 $\mu\text{g m}^{-3}$ in PM_{10} and $\text{PM}_{2.5}$. A further study by (Narukawa et al., 1999) concluded that individual haze particles over Kalimantan of Indonesia were mainly composed of water soluble organic materials and inorganic salt such as ammonium sulphate.

The ionic organic compounds (including carboxylic, dicarboxylic and ketoacids) were distributed between both sub-micron and super micron mode, indicating origins in both gas-to-particle conversion and heterogeneous reaction on pre-existing particles. WSOC in atmospheric aerosols and droplets can be divided by their functional groups into three classes which are neutral, mono- and dicarboxylic acid and also polycarboxylic acid, which

were found to account on average for 87% of total fine aerosol WSOC (Decesari et al., 2000). The most frequently determined WSOC are the low molecular weight (LMW) carboxylic and dicarboxylic acids (Yu, 2000). Most of carboxylic acids compound are a secondary oxidation products of atmospheric organic compounds and also found in remote marine as well as continental rural and urban areas (Simoneit and Mazurek, 1982). Among these dicarboxylic acids (DCA's), oxalic acid is the most abundant, followed by succinic and malonic in atmospheric aerosol especially during summer season.

In the aqueous phase, organic oxidation also can be initiated by various radical anions in the atmosphere (e.g. $\text{OH}\cdot$, NO_3^- , SO_4^{2-} , $\text{Cl}\cdot$). Among these species, it is very likely that $\text{OH}\cdot$ is the most efficient initiating organic oxidation (Dutot et al., 2003). The DCA's are the late products in the photochemistry of aliphatic and aromatic hydrocarbons, and due to the low vapour pressure, it is almost entirely partitioned to the particulate phase. They also constitute an important fraction of the water soluble part of particulate organic matter (POM) in atmospheric aerosol particles at remote and urban areas (Rohrl and Lammel, 2001).

3. Dicarboxylic acids

During the past decade, much attention has been paid to the low molecular weight dicarboxylic acids and related polar compounds which are ubiquitous water-soluble organic compounds that have been detected in a variety of environmental samples including atmospheric aerosols, rainwaters, snow packs, ice cores, meteorites, marine sediments, hypersaline brines and freshwaters (Kawamura and Ikushima, 1993; Tedetti et al., 2006). In the atmosphere, dicarboxylic acids originate from incomplete combustion of fossil fuels (Kawamura and Ikushima, 1993; Kawamura and Kaplan, 1987), biomass burning (Narukawa et al., 1999), direct biogenic emission and ozonolysis and photo-oxidation of organic compound (Sempere and Kawamura, 2003).

Low molecular weight (LMW) dicarboxylic acids have also been identified in cloud water samples collected at a high mountain range in central Europe (Puxbaum and Limbeck, 2000), in the condensed phase at a semi-urban site in the northeastern US (Khwaja, 1995) and in Arctic aerosol (Kawamura et al., 1996). As a result of their hygroscopic properties, dicarboxylic acids can act as cloud condensation nuclei and have an impact on the radiative forcing at earth's surface (Kerminen et al., 2000). Dicarboxylic acids also participate in many biological processes. They are important intermediates in the tricarboxylic acid and glyoxylate cycles and the catabolism and anabolism of amino acids (Tedetti et al., 2006).

Photochemical reactions are also an important source of atmospheric dicarboxylic acids. For example, glutaric acids photooxidation is likely the dominant pathway formation, as measured atmospheric concentrations of dicarboxylic acids in Los Angeles far surpasses contributions from direct emissions and seasonal trends suggest that dicarboxylic acids are largely produced in photochemical smog (Puxbaum and Limbeck, 2000; Rogge et al., 1993).

Aliphatic dicarboxylic acids (or diacids) can be described by the following general formula:



According to IUPAC nomenclature, dicarboxylic acids are named by adding the suffix dioic acid to the name of the hydrocarbon with the same number of carbon atoms, e.g., nonanedioic acid for $n=7$. The older literature often uses another system based on the hydrocarbon for the $(\text{CH}_2)_n$ carbon segment and the suffix dicarboxylic acid, e.g., heptanedicarboxylic acid for $n=7$. However, trivial names are commonly used for the saturated linear aliphatic dicarboxylic acids from $n=0$ (oxalic acid) to $n=8$ (sebacic acid) and for the simple unsaturated aliphatic dicarboxylic acids; these names are generally derived from the natural substance in which the acid occurs or from which it was first isolated.

Aliphatic dicarboxylic acids are found in nature both as free acids and as salts. For example, malonic acid is present in small amounts in sugar beet and in the green parts of the wheat plant; oxalic acid occurs in many plants and in some minerals as the calcium salt. However, natural sources are no longer used to recover these acids.

The main industrial process employed for manufacturing dicarboxylic acids is the ring-opening oxidation of cyclic compounds.

Oxalic acid is the most important dicarboxylic acid. Adipic, malonic, suberic, azelaic, sebacic, and 1,12-dodecanedioic acids, as well as maleic and fumaric acids, are also manufactured on an industrial scale.

Physical properties: Dicarboxylic acids are colorless, odorless crystalline substances at room temperature. Table 1 lists the major physical properties of some saturated aliphatic dicarboxylic acids.

The lower dicarboxylic acids are stronger acids than the corresponding monocarboxylic ones. The first dissociation constant is considerably greater than the second. Density and dissociation constants decrease steadily with increasing chain length. By contrast, melting point and water solubility alternate: Dicarboxylic acids with an even number of carbon atoms have higher melting points than the next higher odd-numbered dicarboxylic acid. In the $n=0-8$ range, dicarboxylic acids with an even number of carbon atoms are slightly soluble in water, while the next higher homologues with an odd number of carbon atoms are more readily soluble. As chain length increases, the influence of the hydrophilic carboxyl groups diminishes; from $n=5$ (pimelic acid) onward, solubility in water decreases rapidly. The alternating solubility of dicarboxylic acids can be exploited to separate acid mixtures. Most dicarboxylic acids dissolve easily in lower alcohols; at room temperature, the lower dicarboxylic acids are practically insoluble in benzene and other aromatic solvents.

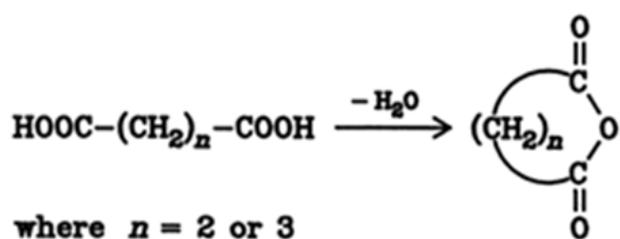
IUPAC name	Common name	Formula	Molecular weight, M_r	Melting point, M_p , °C	Boiling point, B_p , at 13.3 kPa, °C	Density, ρ , at 25°C, g/cm ³	Solubility in mol/kg	Ionisation constant	
								K_1	K_2
Ethanedioic acid	Oxalic acid	HOOC-COOH	90.03	189.5	-	1.653	1.131	5.29×10^{-2}	5.33×10^{-5}
Propanedioic acid	Malonic acid	HOOC-CH ₂ -COOH	104.06	135	-	1.619	16.03	1.42×10^{-3}	2.01×10^{-6}
Butanedioic acid	Succinic acid	HOOC-(CH ₂) ₂ -COOH	118.08	188	235	1.572	0.748	6.16×10^{-5}	2.31×10^{-6}
Pentanedioic acid	Glutaric acid	HOOC-(CH ₂) ₃ -COOH	132.11	99	200	1.424	8.468	4.57×10^{-5}	3.89×10^{-6}
Hexanedioic acid	Adipic acid	HOOC-(CH ₂) ₄ -COOH	146.14	153	265	1.360	0.171	3.85×10^{-5}	3.89×10^{-6}
Heptanedioic acid	Pimelic acid	HOOC-(CH ₂) ₅ -COOH	160.17	106	272	1.329	0.423	3.19×10^{-5}	3.74×10^{-6}
Octanedioic acid	Suberic acid	HOOC-(CH ₂) ₆ -COOH	174.19	144	279	1.266	0.0139	3.05×10^{-5}	3.85×10^{-6}
Nonanedioic acid	Azelaic acid	HOOC-(CH ₂) ₇ -COOH	188.22	108	287	1.225	0.00946	2.88×10^{-5}	3.86×10^{-6}
Decanedioic acid	Sebacic acid	HOOC-(CH ₂) ₈ -COOH	202.25	134.5	-	1.207	0.00012	3.1×10^{-5}	3.6×10^{-6}

Table 1. Physical properties of saturated dicarboxylic acid (Clarke, 1986)

Chemical properties: The chemical behavior of dicarboxylic acids is determined principally by the two carboxyl groups. The neighboring methylene groups are activated generally to only a minor degree. Thermal decomposition of dicarboxylic acids gives different products depending on the chain length. Acids with an even number of carbon atoms require higher decarboxylation temperatures than the next higher odd-numbered homologues; lower dicarboxylic acids decompose more easily than higher ones. To avoid undesired decomposition reactions, aliphatic dicarboxylic acids should only be distilled in vacuum. When heated above 190 °C, oxalic acid decomposes to carbon monoxide, carbon dioxide, and water. Malonic acid is decarboxylated to acetic acid at temperatures above 150 C:



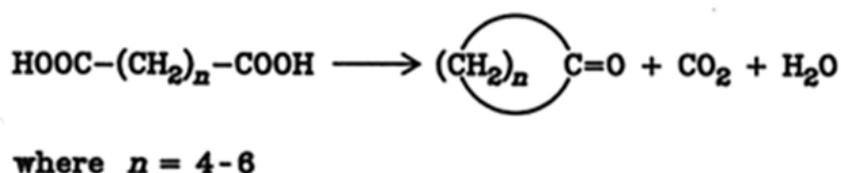
When malonic acid is heated in the presence of P_2O_5 at ca. 150 °C, small amounts of carbon suboxide (C_3O_2) are also formed. Succinic and glutaric acids are converted into cyclic anhydrides on heating:



Scheme 1. Succinic and glutaric acids are converted into cyclic anhydrides on heating

When the ammonium salt of succinic acid is distilled rapidly, succinimide is formed, with the release of water and ammonia.

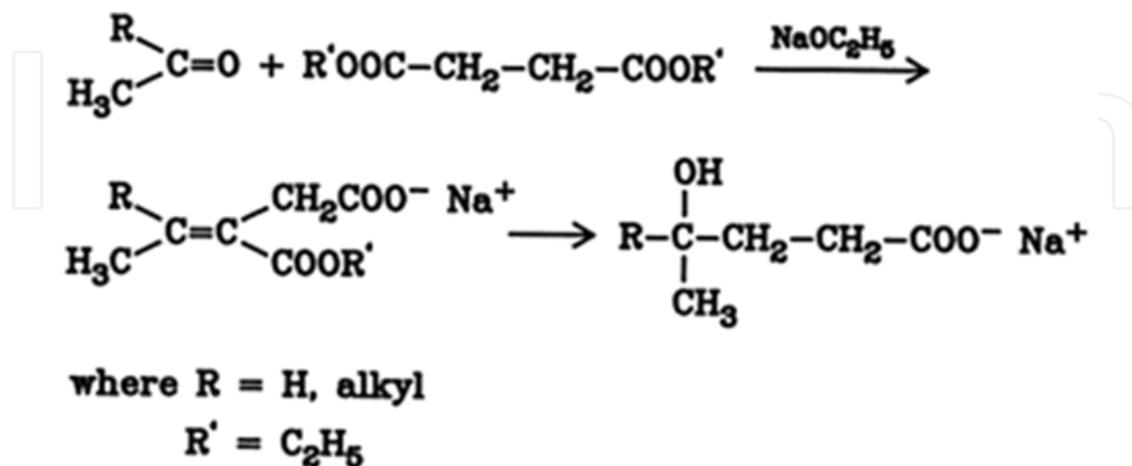
Higher dicarboxylic acids from $n = 4$ (adipic acid) to $n = 6$ (suberic acid) split off carbon dioxide and water to form cyclic ketones:



Scheme 2. Higher dicarboxylic acids from $n = 4$ (adipic acid) to $n = 6$ (suberic acid) split off carbon dioxide and water to form cyclic ketones

The decomposition of still higher dicarboxylic acids leads to complex mixtures. With the exception of oxalic acid, dicarboxylic acids are resistant to oxidation. Oxalic acid is used as a reducing agent for both commercial and analytical purposes. Dicarboxylic acids react with dialcohols to form polyesters and with diamines to form polyamides. They also serve as starting materials for the production of the corresponding diamines. Reaction with monoalcohols yields esters. All of these reactions are commercially important. Several reactions with malonic and glutaric acids are of interest in organic syntheses: the Knoevenagel condensation, Michael addition, and malonic ester synthesis (Clarke, 1986)

Succinic acid ester reacts with aldehydes or ketones in the presence of sodium ethoxide or potassium *tert*-butoxide to form alkylidenesuccinic acid monoesters (Stobbe condensation). These can subsequently be converted into monocarboxylic acids by hydrolysis, decarboxylation, and hydrogenation (Clarke, 1986).



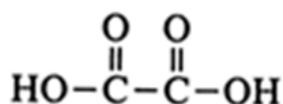
Scheme 3. Production number of straight-chain aliphatic dicarboxylic acids and their derivatives occur in nature

Production: A number of straight-chain aliphatic dicarboxylic acids and their derivatives occur in nature. However, isolation from natural substances has no commercial significance. Although many syntheses for the production of aliphatic dicarboxylic acids are known, only a few have found industrial application. This is due partly to the shortage of raw materials.

Individual saturated dicarboxylic acids: Dicarboxylic acids are used mainly as intermediates in the manufacture of esters and polyamides. Esters derived from monofunctional alcohols serve as plasticizers or lubricants. Polyesters are obtained by reaction with dialcohols. In addition, dicarboxylic acids are employed in the manufacture of hydraulic fluids, agricultural chemicals, pharmaceuticals, dyes, complexing agents for heavy-metal salts, and lubricant additives (as metal salts).

3.1. Oxalic acid

Oxalic acid (ethanedioic acid, acidum oxalicum) is the simplest saturated dicarboxylic acid (Clarke, 1986). The compound exists in anhydrous form [144-62-7] or as a dihydrate [6153-56-6]. The anhydrous acid is not found in nature and must be prepared from the dihydrate even when produced industrially. Oxalic acid is widely distributed in the plant and animal kingdom (nearly always in the form of its salts) and has various industrial applications.



Scheme 4. Chemical structure of oxalic acid

The acidic potassium salt of oxalic acid is found in common sorrel (Latin: *oxalis acetosella*) and the name oxalic acid is derived from that plant. Table 2 shows examples of plants in which oxalic acid occurs (in the form of potassium, sodium, calcium, magnesium salts, or iron complex salts) are given below (oxalic acid content in milligrams per 100 g dry weight):(Tsu-Ning Tsao G., 1963)

Spinach	460 – 3200
Rhubarb	500 – 2400
Chard	690
Parsley	190
Beets	340
Cocoa	4500
Tea	3700
Beet leaves	up to 12 000

Table 2. Oxalic acid content in milligrams per 100 g dry weight

Oxalic acid is formed in plants through incomplete oxidation of carbohydrates, e.g., by fungi (*Aspergillus niger*) or bacteria (*acetobacter*) and in the animal kingdom through carbohydrate metabolism via the tricarboxylic acid cycle. The urine of humans and of most mammals also contains a small amount of calcium oxalate. In pathological cases, an increased calcium oxalate content in urine leads to the formation of kidney stones (Clarke, 1986). Calcium and iron(II) oxalates are also found as minerals. Both the anhydrous and dihydrated forms of oxalic acid form colorless and odorless crystals.

Anhydrous oxalic acid

Anhydrous oxalic acid [144-62-7] exists as rhombic crystals in the *a*-form and as monoclinic crystals in the *b*-form (West, 1980). These forms differ mainly in their melting points. The slightly stable *b*-form changes into the *a*-form at 97 °C and 0.2 barr. Anhydrous oxalic acid is prepared by dehydration of the dihydrate through careful heating to 100 °C. It is then sublimated in a dry air stream. The sublimation is fast at 125 °C and can be carried out at temperatures up to 157 °C without decomposition. The dehydration can also be accomplished by azeotropic distillation with benzene or toluene. Anhydrous oxalic acid is slightly hygroscopic; it absorbs water from moist air (“weathers”) to form the dihydrate again. The hydration occurs very slowly because of surface caking.

Oxalic acid dihydrate

Oxalic acid dihydrate [6153-56-6], $\text{HOOC-COOH} \cdot 2 \text{H}_2\text{O}$ is the industrially produced and usual commercial form of oxalic acid. The compound forms colorless and odorless prisms or granules that contain 71.42 wt % oxalic acid and 28.58 wt % water. Oxalic acid dihydrate is stable at room temperature and under normal storage conditions. The most important physical properties are as follows:

The solubility in water and the density of these solutions are presented in Table.1. Oxalic acid is readily soluble in polar solvents such as alcohols (although partial esterification occurs), acetone, dioxane, tetrahydrofuran, and furfural. Oxalic acid is sparingly soluble in diethyl ether (1.5 g oxalic acid dihydrate in 100 g ether at 25 °C), and insoluble in benzene, chloroform, and petroleum ether. The ionization constants show that oxalic acid is a strong acid. The value of K_1 is comparable to that of mineral acids and the value of K_2 corresponds to ionization constants of strong organic acids, for example, benzoic acid.

In the homologous series of dicarboxylic acids, oxalic acid, the first member, shows unique behavior because of the interaction of the neighboring carboxylate groups. This results in an increase in the value of the dissociation constant and in the ease of decarboxylation: Upon rapid heating to 100 °C oxalic acid decomposes into carbon monoxide, carbon dioxide, and water with formic acid as an isolable intermediate.

In aqueous solution decomposition is induced by light and to a much greater extent by γ - or X-rays (to carbon monoxide, carbon dioxide, formic acid, and occasionally hydrogen). This decomposition is catalyzed by the salts of heavy metals, for example, by uranyl salts. Oxalic acid cannot form an intramolecular anhydride. Upon heating to over 190 °C or warming in concentrated sulfuric or phosphoric acid, oxalic acid decomposes to carbon monoxide, carbon dioxide, and water: this decomposition is not exothermic.

The reducing properties of oxalic acid (which itself is oxidized to the harmless end products carbon dioxide and water) form the basis for the variety of practical applications. Oxalic acid is also oxidized relatively easily to carbon dioxide by many other oxidizing agents in addition to air, especially in the presence of the salts of heavy metals. Oxalic acid is easily esterified, whereby two types, the acidic mono or neutral diesters can result. These esters are applied as intermediates in chemical syntheses. They react relatively easily with water, ammonia, or amines to afford the corresponding acyl derivatives.

Important chemical characteristics are also demonstrated by the metal salts of oxalic acid. These exist in two types-the acidic and neutral salts. The alkali metal and iron (III) salts are readily soluble in water. All other salts are sparingly soluble in water. The near complete insolubility of the alkaline-earth salts of oxalic acid, especially of calcium oxalate, finds some applications in quantitative analysis. When heated all these metal salts lose carbon monoxide. Other salts which are easier decomposable lose carbon dioxide in addition. The alkali and alkaline-earth salts form carbonates under these conditions. Manganese, zinc, and tin salts form oxides; iron, cadmium, mercury, and copper salts form mixtures of oxides and metals. Nickel, cobalt, and silver salts afford pure metals. Anhydrous fusion of oxalates with alkali yield carbonates and hydrogen. For a review see Dollimore (1987).

3.2. Malonic acid

Three-carbon 1,3-dicarboxylic acid derivatives (malonic acid, malonates, cyanoacetic acid, cyanoacetates, and malononitrile) are widely used in industry for the manufacture of pharmaceuticals, agrochemicals, vitamins, dyes, adhesives, and fragrances. The common

feature of malonic acid and its derivatives is the high reactivity of the central methylene group. Due to the increasingly electron-withdrawing character of the substituents, the acidity of the hydrogen atoms in the 2-position increases in the order malonates < cyanoacetates < malononitrile. Therefore, all these compounds undergo reactions typical of 1,3-dicarbonyl compounds. For example they are easily alkylated or arylated, undergo aldol and Knoevenagel condensations, and they can be used for the synthesis of pyrimidines and other nitrogen heterocycles.

Physical Properties: Important physical properties of malonic acid (propanedioic acid, methanedicarboxylic acid) are listed in Table 1. Its pK_a values are 2.83 and 5.70. Malonic acid forms a colorless hygroscopic solid which sublimes in vacuum with some decomposition. It's really soluble in the water; but slightly soluble in ethanol and diethyl ether, and is completely insoluble in benzene.

Chemical Properties: Malonic acid is found in small amounts in sugar beet and green wheat, being formed by oxidative degradation of malic acid. Reaction with sulfonyl chloride or bromine gives mono- and dihalogenated malonic acid, whereas treatment with thionyl chloride or phosphorus pentachloride leads to mono- or diacyl chloride. When heated with phosphorus pentoxide, malonic acid does not form an anhydride but rather carbon suboxide, a toxic gas that reacts violently with water to reform malonic acid. On heating the free acid above 130 °C, or an aqueous solution above 70 °C, decomposition to acetic acid and carbon dioxide takes place. The mono- and dianion of malonic acid are more stable. In aqueous solution the monosodium salt decomposes above 90 °C and the disodium salt above 130 °C (Bolton, 1995).

3.3. Succinic acid

Succinic acid is found in amber, in numerous plants (e.g., algae, lichens, rhubarb, and tomatoes), and in many lignites.

Production: A large number of syntheses are used to manufacture succinic acid. Hydrogenation of maleic acid, maleic anhydride, or fumaric acid produces good yields of succinic acid; the standard catalysts are Raney nickel, Cu, NiO, or CuZnCr, Pd – Al₂O₃, Pd – CaCO₃, or Ni – diatomite. 1,4-Butanediol can be oxidized to succinic acid in several ways: (1) with O₂ in an aqueous solution of an alkaline-earth hydroxide at 90 – 110 °C in the presence of Pd – C; (2) by ozonolysis in aqueous acetic acid; or (3) by reaction with N₂O₄ at low temperature. Succinic acid or its esters are also obtained by Reppe carbonylation of ethylene glycol, catalyzed with RhCl₃ – pentachlorothiophenol; Pd-catalyzed methoxycarbonylation of ethylene; and carbonylation of acetylene, acrylic acid, dioxane, or β - propiolactone (Bolton, 1995).

Acid mixtures containing succinic acid are obtained in various oxidation processes. Examples include the manufacture of adipic acid; the oxidation of enanthic acid and the ozonolysis of palmitic acid. Succinic acid can also be obtained by phase-transfer-catalyzed reaction of 2-haloacetates, electrolytic dimerization of bromoacetic acid or ester, oxidation of 3-cyanopropanal, and fermentation of *n*-alkanes.

Uses: Succinic acid is used as a starting material in the manufacture of alkyd resins, dyes, pharmaceuticals, and pesticides. Reaction with glycols gives polyesters; esters formed by reaction with monoalcohols are important plasticizers and lubricants (Bolton, 1995).

3.4. Glutaric acid

Glutaric acid occurs in washings from fleece and, together with malonic acid, in the juice of unripened sugar beet.

Production: Glutaric acid is obtained from cyclopentane by oxidation with oxygen and cobalt (III) catalysts or by ozonolysis; and from cyclopentanol – cyclopentanone by oxidation with oxygen and $\text{Co}(\text{CH}_3\text{CO}_2)_2$, with potassium peroxide in benzene, or with N_2O_4 or nitric acid. Like succinic acid, glutaric acid is formed as a byproduct during oxidation of cyclohexanol – cyclohexanone. Other production methods include reaction of malonic ester with acrylic acid ester, carbonylation of γ -butyrolactone, oxidation of 1,5-pentanediol with N_2O_4 , and oxidative cleavage of γ -caprolactone.

Uses: The applications of glutaric acid, e.g., as an intermediate, are limited. Its use as a starting material in the manufacture of maleic acid has no commercial importance.

3.5. Adipic acid

Adipic acid, hexanedioic acid, 1,4-butanedicarboxylic acid, $\text{C}_6\text{H}_{10}\text{O}_4$, M_r 146.14, $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ [124-04-9], is the most commercially important aliphatic dicarboxylic acid. It appears only sparingly in nature but is manufactured worldwide on a large scale. The historical development of adipic acid was reviewed in 1997 (Luedeke, 1997)

Physical properties: Adipic acid is isolated as colorless, odorless crystals having an acidic taste. It is very soluble in methanol and ethanol, soluble in water and acetone, and very slightly soluble in cyclohexane and benzene. Adipic acid crystallizes as monoclinic prisms from water, ethyl acetate, or acetone/petroleum ether.

Chemical properties: Adipic acid is stable in air under most conditions, but heating of the molten acid above 230 – 250 °C results in some decarboxylation to give cyclopentanone [120-92-3], *bp* 131 °C. The reaction is markedly catalyzed by salts of metals, including iron, calcium, and barium. The tendency of adipic acid to form a cyclic anhydride by loss of water is much less pronounced compared to glutaric or succinic acids.

Adipic acid readily reacts at one or both carboxylic acid groups to form salts, esters, amides, nitriles, etc. The acid is quite stable to most oxidizing agents, as evidenced by its production in nitric acid. However, nitric acid will attack adipic acid autocatalytically above 180 °C, producing carbon dioxide, water, and nitrogen oxides.

Use: Adipic acid has been used in the manufacture of mono- and diesters as well as polyamides. Nylon 6,8 is obtained by reaction of suberic acid with hexamethylenediamine, and nylon 8,8 by reaction with octamethylenediamine. Polyamides of adipic acid with

diamines such as 1,3-bis(aminomethyl)benzene, 1,4(bisaminomethyl)cyclohexane, and bis(4-aminocyclohexyl)methane are also of commercial interest. Esters of adipic acid with mono- and bifunctional alcohols are used as lubricants.

4. Dicarboxylic acids distributions in the atmosphere

Numerous organic compounds significantly contribute to the aerosol load of the atmosphere and thus to the radiative forcing of climate. Among others the influence of organic aerosol on cloud droplet formation is a key point in evaluating effects of anthropogenic emissions on climate. In contrast to sulfate more uncertainties exist about organics and in particular for secondary organic aerosol species which are more oxygenated and hygroscopic than primary organic species (Saxena and Hildemann, 1996). Among oxygenated organic species, dicarboxylic acids are probably the best quantified species, though they represent a small fraction of the total organic mass (Kawamura and Ikushima, 1993). Glutaric and malonic acid the atmosphere have potential to increase the cloud condensation nuclei (CCN) activation of major inorganic aerosol such as ammonium sulfate (Cruz and Pandis, 1998). These findings suggest a potentially important role played by dicarboxylic acids on radiative forcing and stimulate their studies since the sources of diacids in the atmosphere remain poorly understood and quantified.

Whatever the region; urban and continental, or remote marine (see Figure 1 which carried out from Table 3), oxalic acid (C₂: HOCCOOH) is always found to be the most abundant diacid followed by succinic (C₄: HOOC(CH₂)₂COOH) and/or malonic (C₃: HOOCCH₂COOH) acid with concentrations of several hundreds of nanograms per cubic meter in urban and continental regions (Kawamura and Ikushima, 1993; Kawamura and Kaplan, 1987) to a few tens of nanograms per cubic meter in remote marine boundary layer (Kawamura and Sakagushi, 1999; Sempere and Kawamura, 2003). In Europe, the most continuous study of diacids was conducted over one year by Limbeck et al., (2005) at Vienna, Austria. Although available data on diacids are more sparse at midlatitudes in Europe, they tend to show that oxalic acid levels at nonurban or rural sites are not considerably different from those at urban sites (Limbeck and Puxbaum, 1999; Rohrl and Lammel, 2001).

Motor exhausts have been proposed to be primary sources of oxalic, malonic, succinic, and glutaric (C₅: HOOC(CH₂)₃COOH) acids (Grosjean et al., 1978; Kawamura and Kaplan, 1987). Some of these diacids are also emitted by wood burning, particularly malonic acid (pine wood) and succinic acid (oak wood) (Rogge et al., 1991; Rogge et al., 1993). Note that until now no direct source of malic (hydroxysuccinic: hC₄: HOOCCH₂CHOHCOOH) and tartaric (dihydroxysuccinic: dhC₄: HOOC(CHOH)₂COOH) acids has been identified.

Glutaric, succinic, and adipic (C₆: HOOC(CH₂)₄COOH) acids have been identified in laboratory studies (Hatakeyama et al., 1985) as secondary organic aerosol products of the reaction of O₃ with cyclohexene, a symmetrical alkene molecule similar to monoterpenes emitted by the biosphere. Hatakeyama et al. (1985) also suggested that malonic and oxalic acids are also produced in the cyclohexene-ozone system.

Unsaturated fatty acids with a double bond at the C₉ position like cis-9-octadecenoic (oleic) acid are oxidized into C₉ diacid (azelaic acid) and other products hereafter mainly oxidized into shorter diacids (Kawamura and Ikushima, 1994; Kawamura and Kaplan, 1987; Kawamura et al., 1985). These unsaturated acids which are abundant in marine phytoplankton and terrestrial higher plant leaves are also emitted by anthropogenic sources such as meat cooking (Rogge, 1991; Rogge et al., 1998) and wood burning processes (Rogge et al., 1998).

Warneck suggested that in the marine atmosphere clouds generate oxalic acid from glyoxal formed by oxidation of acetylene and glycolaldehyde formed by oxidation of ethane (Warneck, 2000). Note that along these processes glyoxylic acid (CHOCOOH) represents a key intermediate (see figure 3) whereas diacids other than oxalic acid are not produced. The formation of dicarboxylic acids in the continental atmosphere (Ervens et al., 2004a) involves production of glyoxal from toluene and of glycolaldehyde from isoprene as well as aqueous phase reactions of adipic and glutaric acids produced by oxidation of cyclohexene. Recently more literature has become available on the formation of oxalic acid that includes also the oxidation of methylglyoxal, an oxidation product of toluene and isoprene, via intermediate steps involving pyruvic and acetic acids (Lim et al., 2005). Since this diacid production pathway also forms oligomers, the knowledge of the sources of diacids is also of importance for the understanding of secondary organic aerosol formation.

The relative contribution of primary and secondary sources of diacids in the atmosphere remains poorly understood. Even though it is agreed that they are likely to be mainly secondary in origin it is not known in which proportion their precursors come from anthropogenic and biogenic sources.

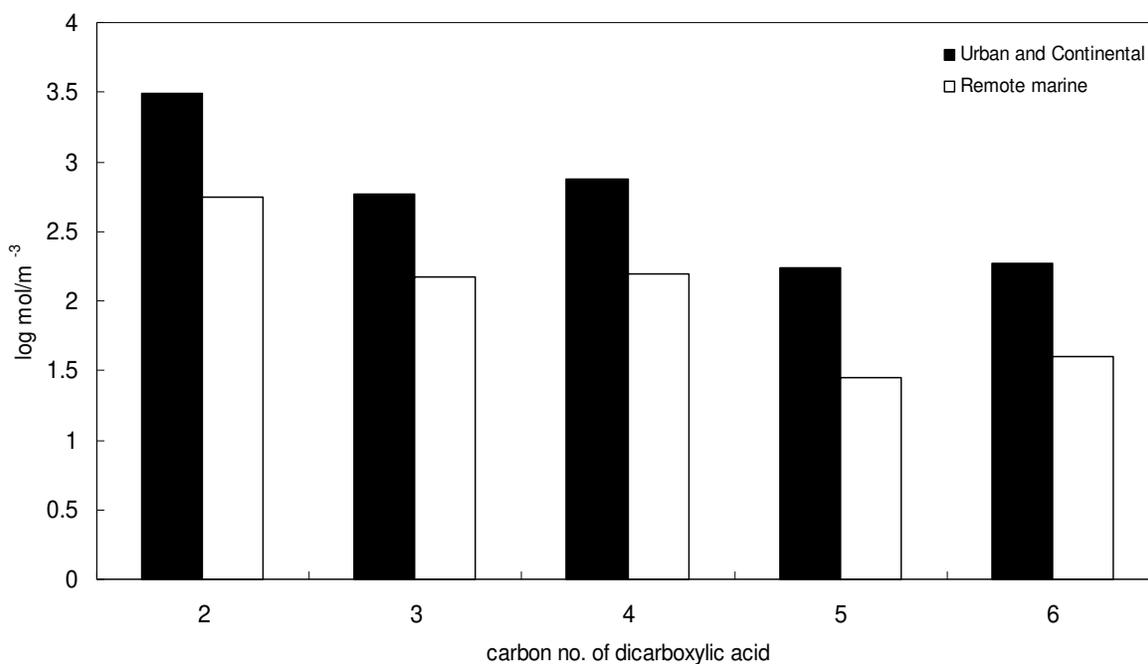


Figure 2. Comparison of dicarboxylic acids distribution in urban/continental and remote marine based on the data collection on table 3

References	Location	Oxalic	Malonic	Succinic	Glutaric	Adipic
(Grosjean et al., 1978)	New York	0	3.6	21.8	17.2	13.2
(Grosjean et al., 1978)	New York	0	3.9	24.9	23.2	11.6
(Kawamura and Kaplan, 1987)	West LA	6.38	1.58	1.96	0.6	2.22
(Kawamura and Kaplan, 1987)	West LA	2.12	0.4	0.66	0.22	0.94
(Kawamura and Kaplan, 1987)	West LA	8.13	0.72	2.34	0.66	3.31
(Kawamura and Kaplan, 1987)	West LA	8.65	1.45	2.37	0.74	0.49
(Kawamura and Kaplan, 1987)	Down Town LA	6.21	0.71	1.19	0.52	0.1
(Kawamura and Kaplan, 1987)	Down Town LA	6.6	0.76	1.84	0.52	0.2
(Kawamura and Kaplan, 1987)	Down Town LA	8.31	1.22	2.13	0.83	0.63
(Sempere and Kawamura, 1994)	Tokyo	29.65	6.69	13.18	3.72	6.66
(Sempere and Kawamura, 1994)	Tokyo	58.89	20.29	28.82	7.54	6.79
(Sempere and Kawamura, 1994)	Tokyo	330	141.3	161.1	4.15	2.91
(Limbeck and Puxbaum, 1999)	South Africa	193	142	58	8.8	7.9
(Limbeck and Puxbaum, 1999)	Sonblick Observatory	153	22	14	2.7	4.4
(Limbeck and Puxbaum, 1999)	Vienna	340	244	117	26	117
(Kawamura and Watanabe, 2004)	Tokyo	357	71.4	73.4	23.1	25.8
(Kawamura and Watanabe, 2004)	Tokyo	157	44	41	11	13
(Kawamura and Watanabe, 2004)	Tokyo	186	40.5	47.4	18.2	14.2
(Rohrl and Lammel, 2001)	Helsinki	0	0	30	0	0
(Ho et al., 2006)	Hong Kong (Road)	478	89.1	71.88	20	10.7
(Ho et al., 2006)	Hong Kong (Road)	268	47.6	33	6.95	12.7
(Hsieh et al., 2007)	Tainan, Taiwan	574	65.8	101	43	13.2
(Hsieh et al., 2007)	Tainan, Taiwan	432	34.2	87.9	10.3	8.8
(Limbeck et al., 2005)	Vienna, Austria	99.6	34	37	7.7	3.3
(Limbeck et al., 2005)	Vienna, Austria	66.2	38.6	30.8	6.6	3.2
(Limbeck et al., 2005)	Vienna, Austria	63.1	21.5	31.2	5.6	2.5
(Limbeck et al., 2005)	Mt Rax, Austria	34.5	9.1	16.4	2.3	0.8
(Limbeck et al., 2005)	Mt Rax, Austria	26.4	6.9	14.9	2.3	4.3
(Limbeck et al., 2005)	Mt Rax, Austria	32.6	16.4	22.4	3	1.7
(Decesari et al., 2006)	Rondonia, Brazil	194.7	73.1	123.5	23.5	14.5
(Decesari et al., 2006)	Rondonia, Brazil	793.3	56.8	210.2	32.1	12.6
(Decesari et al., 2006)	Rondonia, Brazil	937.9	128.5	423.9	34.7	21.2
(Decesari et al., 2006)	Rondonia, Brazil	1260	476.5	667.2	121.1	97.4
(Wang et al., 2006)	Hong Kong (Tunnel)	505	69.4	85.2	20.9	26.4
(Wang et al., 2006)	Hong Kong (Tunnel)	221	34.5	32.7	14.7	13.5
(Wang et al., 2006)	Hong Kong (Tunnel)	234	42	51.4	17.1	24.7
(Wang et al., 2006)	Hong Kong (Tunnel)	312	59.7	62.9	16.7	15.5
(Wang et al., 2006)	Hong Kong (Tunnel)	633	59.3	95.1	30.3	25.9

(a)

References	Location	Oxalic	Malonic	Succinic	Glutaric	Adipic
(Kawamura and Kaplan, 1987)	Green House LA	1.31	0.3	0.29	0.04	0.1
(Kawamura and Kaplan, 1987)	Green House LA	2.83	0.14	0.86	0	0.22
(Kawamura and Sakagushi, 1999)	North Pacific	44.7	23.2	19.5	2.57	3.08
(Kawamura and Sakagushi, 1999)	North Pacific	8.73	2.18	2.16	0.61	1.26
(Kawamura and Sakagushi, 1999)	North Pacific	10.6	1.98	2.22	0.23	2.12
(Kawamura and Sakagushi, 1999)	North Pacific	28.6	12.8	13	1.84	1.34
(Kawamura and Sakagushi, 1999)	North Pacific	667	189	93	20.1	4.9
(Kawamura and Sakagushi, 1999)	North Pacific	190	38.6	16.7	10.2	2.76
(Kawamura and Sakagushi, 1999)	North Pacific	88.5	34.5	21.6	4.72	6.04
(Kawamura and Sakagushi, 1999)	North Pacific	24.9	5.66	10.1	1.87	1.67
(Kawamura and Sakagushi, 1999)	North Pacific	10	2.12	1.52	0.32	0.43
(Kawamura and Sakagushi, 1999)	North Pacific	18.3	3.45	4.02	0.62	0.46
(Kawamura and Sakagushi, 1999)	North Pacific	25.5	5.93	2.99	0.65	0.4
Kawamura (1996)	Antarctic	1.59	0.13	0.63	0.31	0.49
Kawamura (1996)	Antarctic	3.12	0.38	5.77	0.58	0.85
Kawamura (1996)	Antarctic	3.26	0.52	1.18	0.34	0.33
Kawamura (1996)	Antarctic	10.29	2.69	61.53	2.26	1.81
Narukawa(1999)	Indonesia	2200	800.3	1090	310	350
Narukawa(1999)	Indonesia	225	18.4	123	30	40
Khwaja (1994)	semi urban site NY	308	84	55	12	89
Khwaja (1994)	semi urban site NY	245	92	106	16.3	101
Khwaja (1994)	semi urban site NY	118	165	107	15	40
Khwaja (1994)	semi urban site NY	58	81	129	20	21
Khwaja (1994)	semi urban site NY	298	96	90	23	31
Khwaja (1994)	semi urban site NY	1	43	0.5	39	20
Khwaja (1994)	semi urban site NY	360	88	167	46	50
Sempere (2003)	Western Pacific	428.5	78.6	33.4	7.6	7.2
Rohrl (2002)	rural(I)	0	0	14	0	0
Rohrl (2002)	rural(II)	0	0	8.8	0	0
Rohrl (2002)	rural(III)	0	0	18	0	0
(Kawamura et al., 2007)	Canadian arctic	9.89	2.74	2.16	0.54	0.51
(Kawamura et al., 2007)	Canadian arctic	8.3	2.87	1.44	0.37	0.26
(Kawamura et al., 2007)	Canadian arctic	5.26	1.67	1.08	0.22	0.27
(Narukawa et al., 2002)	Arctic,Alert	23.5	5.03	3.21	1.21	0.54
(Narukawa et al., 2002)	Arctic,Alert	40.09	11.6	15.67	2.16	0.55
(Mochida et al., 2007)	North Pacific,ACE	600	110	52	8.9	2
(b)						

Table 3. Summary of aerosol dicarboxylate concentration (ng m^{-3}) in urban/continental (a) remote marine (b) locations

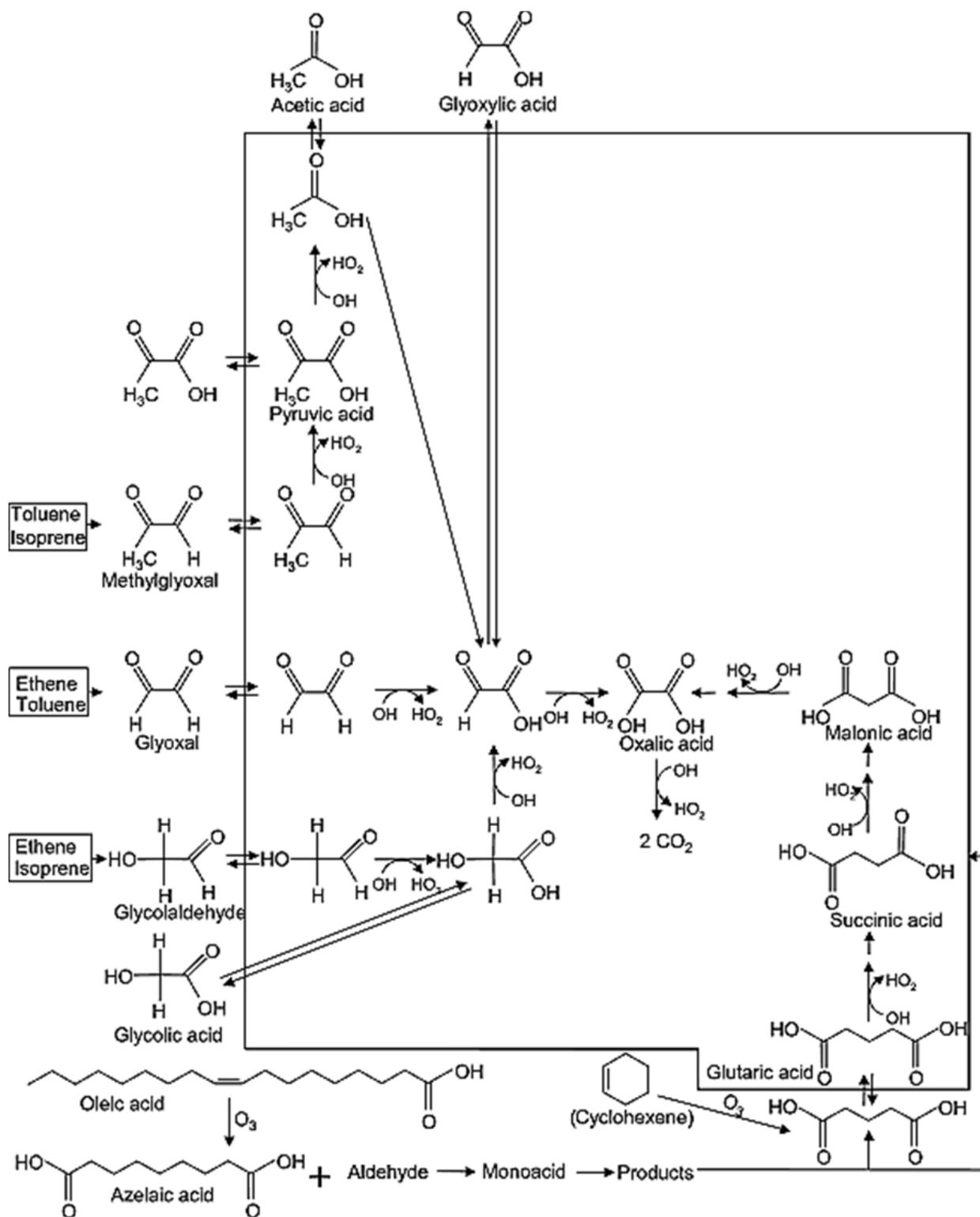


Figure 3. Multiphase organic chemistry producing C₂-C₅ diacids from key biogenic and anthropogenic precursors. The box refers to the aqueous phase. The figure is mainly adapted from (Ervens et al., 2004b) with modifications to account for the reaction pathway methylglyoxal/pyruvic acid/acetic acid/glyoxylic acid suggested by (Lim et al., 2005). In addition to cyclohexene used by (Ervens et al., 2004b) as a model compound for symmetrical alkenes, following (Legrand et al., 2007) we also report the oleic acid degradation into azelaic, C₄ and C₅ diacids.

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