A Review of Household Products Induced Secondary Organic Aerosols Formation in Indoor Environment

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Authors' contributions

This work was carried out in collaboration between all authors. Author JAA wrote the first draft of the manuscript and managed literature searches. Authors LAJ and JAS reviewed and revised successive drafts of the manuscript. All authors read and approved the final manuscript.

Review Article

ABSTRACT

This paper reviews the process of formation of secondary organic aerosols (SOAs) in the indoor environment. SOAs have been found to have more alarming health effects on humans and environment. To be able to assess and quantify the risk, it is important to have a comprehensive information on their mechanism of formation. The photochemical reactions of volatile organic compounds (VOCs) released from the use of the consumer products with ozone (O_3), hydroxyl group (OH^-), and oxides of nitrogen NO_x were considered. Environmental factors such as temperature, relative humidity and light were also found to have impact on the physical and chemical composition of the resulting SOAs. Gas – phase partitioning was identified as responsible for the formation of SOAs. Common health effects associated with SOAs and mitigation measures were suggested.

Keywords: Aerosols; formation; indoor environment; household products; secondary organic aerosols.

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1. INTRODUCTION

A variety of inorganic and organic chemical compounds are present in the particulate phase of aerosols from household consumer products. The organic fraction in aerosols can account for a 20 - 90% of the finest fraction [1] and, therefore, the knowledge of this fraction is important to prevent human health risks associated with them [2]. Both inorganic and organic aerosols can be directly emitted (primary aerosols) or can be formed in the atmosphere as a consequence of multiple physical and chemical processes - secondary aerosols [3,4]. Human exposure to aerosols takes place both in the indoor and outdoor environment [5,6,7]. However, because people spend majority of their time in the indoor environment, exposure to aerosols and the consequent effects on human health have been the topics of research interest in recent years [8,9,10,11].

Domestic aerosol products such as insecticides, air fresheners and perfumes are commonly used all over the world. Domestic aerosols are consumer aerosol products that are dispersed under pressure from disposable containers. Aerosol product has three main components: including the active ingredient(s), the propellant, and miscellaneous additives such as solvents, plasticizers, and emulsifiers which are used to improve the product [12]. Active ingredients in the domestic aerosol products include terpenes. Terpenes and propellants in domestic aerosol products are volatile organic compounds (VOCs) [12,13].

The use of air fresheners and perfumes indoors can cause an increase in the airborne concentrations of gaseous and particulate species in the indoor environment. Terpenes are unsaturated volatile organic compounds that occur in nature and are presumed to be safe. However, many terpenes have been found to have serious health effects [14,15] while concentrations of terpenes emitted from air fresheners are far greater than those found in nature [16]. Terpenes like α-pinene, d-limonene, linalool, and citronellol react with transient compounds in the air [17]. Ozone–terpenes reactions produce carbonyls such as formaldehyde and acetaldehyde, organic acids, hydrogen peroxide, secondary organic aerosol, and hydroxyl (OH) radical [18]. Subsequent reactions of OH group with the terpenes can generate additional particulate matter and VOCs [19]. Investigations have shown that the reaction between ozone and terpenes from air fresheners and perfumes could result in the formation of particulate matter in indoor atmosphere [14,15,16,17,18,19,20,21,22,23].

Most propellants in spraying products are often viewed to be chemically unreactive. However, European Commission report stated that butane and isobutane(used as propellants) in consumer products may contain 1,3-butadiene at a concentration greater than or equal to 0.1% [24,25] established in their study that SOAs may be formed when 1, 3, butadiene photo decompose in the presence of air containing nitric oxide. The aim of the present work is to present a basic overview of how secondary secondary organic aerosols are formed from spraying consumer products and their implications on humans and indoor environment. Some of the existing literatures are reviewed therein to give a clearer picture of the factors and mechanisms involved in SOAs formation.

2. ORGANIC COMPOUNDS IN INDOOR ENVIRONMENT

According to [26,27], organic compounds present in indoor air include very volatile organic compounds (VVOCs), volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs) and non-volatile organic compounds (NVOCs), or organic compounds associated with particulate matter or particulate organic matter (POM) [26]. Table 1 shows the detailed classification of inorganic pollutants as adapted from [26]. VOCs are carbon-based

chemicals which are volatile at normal room temperatures, and whose vapours are readily inhaled [28].

Table 1. Classification of organic pollutants

Description	Abbreviation	Boiling point range (ºC)	Example compounds
Very volatile (gaseous) organic compound	VVOC	< 0 to 50 – 100	Propane , Butane, Methyl chloride
Volatile organic compounds	VOC	50 -100 to 240 – 260	Formaldehyde, d – limonene, toluene, ehanol(ethyl alcohol), 2 – propanol (isopropyl alcohol, hexanal)
Semi volatile organic compounds	SVOC	240 – 260 to 380 – 400	Pesticides(DDT, Chlordane, plastiicizers(phtalates), fire retardants)

Source: WHO [24]

VOCs is an important group of indoor air pollutants whose concentration levels are elevated indoors [24]. Typical boiling points of VOCs are in the range of 50-100ºC [28,29]. According to Wolkoff [28], VOCs comprise a range of substances including alkanes, alkenes, aromatic hydrocarbons, chlorinated hydrocarbons, esters and alcohols (derived in part from microbiological sources), aldehydes and ketones (many from precursor terpene compounds and fatty acids). Products used at home can release VOCs into indoor air when used or stored [31-33]. These VOCs released as a result of solvent and propellants used in consumer aerosol products has been reffered to as reactive organic compounds (ROGs) because of thier high reactivity with the major oxidizing species (O_3, OH^-, and NO_3) present in the atmosphere [34]. ROGs with double bonds (Alkenes, cycloalkenes, dienes, and terpenes) are more reactive and can thus react with the three commonest oxidizing agents present in the atmosphere [34]. The reactivity of ROGs towards the major oxidizing species are as shown in Table 2.

Table 2. Reactivity of ROGs towards oxidizing species in air
(units: cm^3 molecule^{-1} s^{-1} at 289K)

	Ozone	OH radical	NO$_3$ radical
Alkanes, Cycloalkanes	$\leq 10^{-23}$	$0.3 – 8.0 \times 10^{-11}$	$\leq 10^{-17}$
Oxygenated Aliphatics	$\leq 2.2 \times 10^{-21}$	$0.2 – 6.0 \times 10^{-11}$	$\leq 1.4 \times 10^{-16}$
Aromatics	$\leq 6 \times 10^{-11}$	$0.1 – 6.0 \times 10^{-11}$	$\leq 10^{-17}$
Alkenes, cycloalkenes, other olefins	$2 \times 10^{-18} – 1.5 \times 10^{-15}$	$0.8 – 12 \times 10^{-11}$	$6 \times 10^{-17} – 3 \times 10^{-11}$

Source: Grosjean and Seinfeld [33]

EPA's Total Exposure Assessment Methodology (TEAM) studies found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas [35,36]. Additional EPA TEAM studies [37] established that while people are using products

containing organic chemicals, they can expose themselves and others to very high pollutant levels, and elevated concentrations can persist in the air long after the activity is completed. The level of VOCs present in indoor environments is also affected by the phenomenon of so-called secondary emissions [27].

VOCs emitted from the use of consumer spraying products are converted by reaction in photochemical oxidizing agents to form Secondary Organic Aerosols (SOAs) over time. Secondary emission is any process that releases new airborne pollutants from existing sources, changes the total emitted mass of existing pollutants, or results in chemical reactions between compounds on surfaces and those in the air [22].

2.1 Photo – Chemical Reactions of Volatile Organic Compounds

VOCs in consumer spraying products such as terpenes react with OH^-, NO_x and O_3 radicals in the indoor environment to give stable and condense phase compounds which may include the SOAs. Terpenes/ Reactive radicals reaction which results in the formation of SOAs in the presence/ absence of light are highlighted in the following subsections.

2.1.1 Reaction with hydroxyl radicals (OH^-)

Hydroxyl radicals have been known to have a very high reactivity with most indoor atmospheric compounds [38,39,40]. They are present in indoor air at concentrations sufficient enough to react with VOCs [41]. Ozone reacts with unsaturated volatile organic compounds such as d-limonene and α-pinene to give hydroxyl radical as an intermediate product [42].Hydroxyl radicals in turn react with VOCs to form Toxic Air Contaminants such as formaldehyde and acetyldehyde [33,44]. Terpenes have a very high reactivity with OH^- radicals that the oxidation initiated by OH^- produces carbonyls and hydroxycarbonyls, such as glyoxal, methylglyoxal, and glycolaldehyde [43].Taking limonene as an example, the reaction could take the following pattern:

$$\text{Limonene} + O_3 \longrightarrow \text{limonaldehyde} + OH^- \tag{1}$$

2.1.2 Reaction with ozone (O_3)

Ozone enters indoor environments with outdoor air [44] and typically is present indoors at levels that are 10 to 50% of concurrent outdoor levels [45]. Typical indoor-outdoor ozone ratios are 0.2 - 0.7 [45], so peak indoor levels in the range of 30-100 ppb are expected when ambient pollution levels are high [41]. The concentration of O_3 in the indoor air will have a direct effect with number concentration of SOA formed. This can be depicted in Fig. 1.
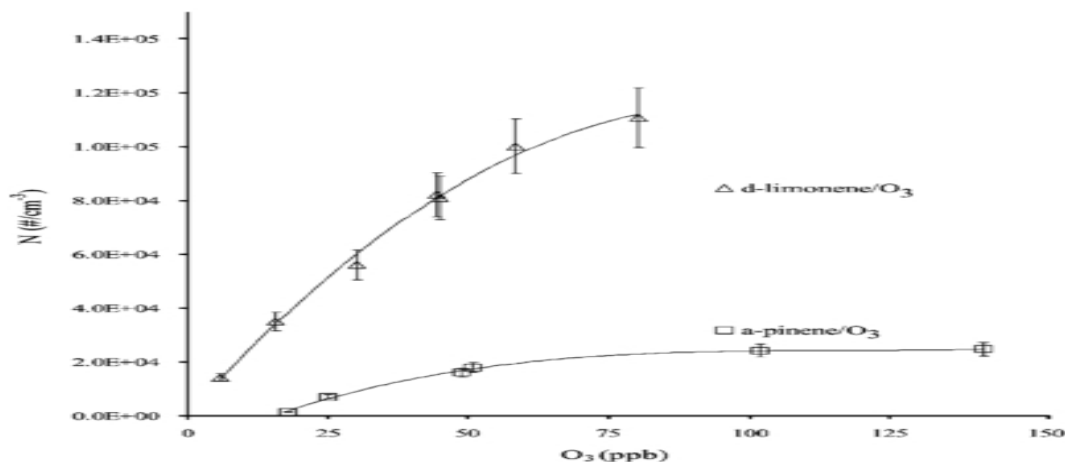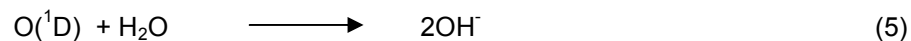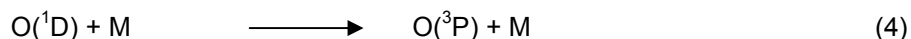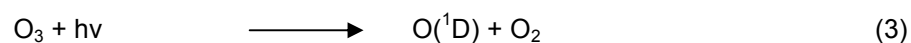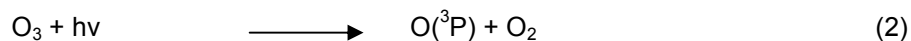
Fig. 1. Effect of O_3 concentration on particle concentration
Source: Nøjgaard et al. [44]

The figure shows the total particle concentration following 60 min of ozonolysis of d-limonene and α-pinene in the absence of NO_2. The experiments were conducted in 1000 l teldar bags to study the effects of the nitrogen dioxide (NO_2) concentration on particle formation during ozonolysis of two abundant monoterpenes indoors, a-pinene and d-limonene at $21\pm2°C$ and atmospheric pressure. The nucleation potential of NO_2 was found to be much lower than ozone. Therefore, the role of O_3 in SOA formation was more significant as compared to NO_2. The result indicated that particle concentrations from ozonolysis of the monoterpenes do not depend on O_3 concentration linearly [46]. Table 3 summarizes the half-life for each of a number of processes that affect the ozone concentration indoors. Findings have also revealed that ozone are released indoor as a result of the use of electrical equipment [11,47,48,49,50,51]. In the pesence of light, O_3 photodecompose to give OH^- radical.

$$O_3 + hv \longrightarrow O(^3P) + O_2 \tag{2}$$

$$O_3 + hv \longrightarrow O(^1D) + O_2 \tag{3}$$

$$O(^1D) + M \longrightarrow O(^3P) + M \tag{4}$$

$$O(^1D) + H_2O \longrightarrow 2OH^- \tag{5}$$

M is a neutral third body usually N_2 or O_2 [49].

Terpenes, such as d-limonene and α-pinene, are common VOC constituents of products that are used indoors. Constituents of consumer household spraying products react with ozone, which is considered a good initiator for indoor gas – phase oxidation process [32,41,52,53]. The type of SOAs formed from this process is termed ozonolysis product [54,55,56,57,58,59].

$$Terpenes + O_3 \longrightarrow Ozonolysis\ Product \tag{6}$$

O_3 reacts considerably faster with VOCs containing unsaturated carbon-carbon bonds. Taatjes et al. [60] pointed out that ozonolysis products also known as ozonides formed from

ozone- terpenes reaction are unstable and may easily decompose. The unstable products were termed Criegee intermediates (CH_2OO) [61,62,63]. Criegee intermediates may undergo decomposition such that it will yield hydroxyl radical [60]. Aschmann et al. [58] the described process using hydroperoxide channel. The reactions are as follow:

$$R1CH_2C(R2)OO^* \rightarrow [R1CH=C(R2)OOH] \rightarrow R1CHC(O)R2 + OH \tag{7}$$
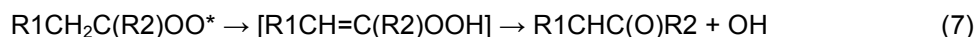
On reaction with water vapour, it yields α-hydroxyhydroperoxides

$$R1CH_2C(R2)OO^* + H_2O \rightarrow R1CH_2C(R2)(OH)OOH \tag{8}$$
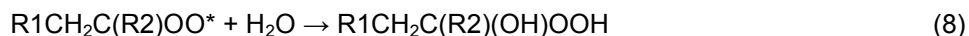
Table 3. Half-Life of indoor ozone for a number of processes

Process	Rate coefficient	Range of Half – Lives (min)
Air Exchange rates	0.2-2.0 (h^{-1})	21 – 210
Removal by surfaces	1.4 – 7.6 (h^{-1})	6 – 30
Reaction with limonene	4.9 x 10^{-6}($ppb^{-1}s^{-1}$)	60 – 500
Reaction with α-pinene	2.1 x 10^{-6}($ppb^{-1}s^{-1}$)	130 – 1100

Source: EC [61]

2.1.3 Reaction with NO_x

SOAs can either be formed in the presence of NO_x or in their absence [64,65,66,67]. SOAs growth is affected by NO_x concentration in indoor air [41,68]. Few investigations have shown that more SOAs are formed under high NO_x conditions [40,41,42,43,67]. However, more experiments have shown that low NO_x condition will favour SOAs formation [68,69,70,71,72,73]. The proportoinality of low NO_x has also been investigated and buttressed using computational simulation [74]. EC [61] showed that when the concentration of NO_2 and O_3 are high, the reaction could proceed as follow:

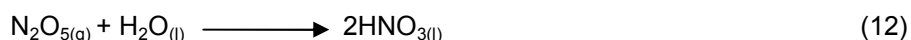$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \tag{9}$$

And also,
NO_3 reacts with rapidly with NO to give NO_2:

$$NO_3 + NO \longrightarrow 2NO_2 \tag{10}$$

When NO concentration is low,

$$NO_3 + NO_2 \longleftrightarrow N_2O_5 \text{ (dinitrogen pentoxide)} \tag{11}$$

N_2O_5 could react with moist surface to give HNO_3 as indicated in the following reaction

$$N_2O_{5(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(l)} \tag{12}$$

In the presence of light, the reaction could also follow this pattern:

$$NO_2 + h\nu \longrightarrow NO + O \tag{13}$$

$$O + O_2 + M \longrightarrow O_3 \tag{14}$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{15}$$
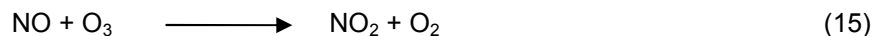
2.2 Secondary Organic Aerosols (SOA)

The aerosols directly emitted into the atmosphere from the source are named primary aerosols while those formed through a series of reactions in the atmosphere are called secondary aerosols [75,76,77]. SOA is an organic liquid or solid particle suspended in the air, which is formed through photochemical reactions of VOCs or primary aerosols. Investigations [14,23]have shown that the reaction between ozone and terpenes are responsible for formation of particulate matter indoor with limonene and α – pinene as most reactive compounds. Clausen et al. [18] investigated indoor ozone/terpenes reaction in a ventilated apartment under normal conditions. The result of their investigation showed that even under normal condition of temperature between 22–25ºC, relative humidity of between 32–40% and average air exchange rate of between 0.7 and 0.8/h, high particle concentration could be formed. Some of the previous studies on the formation of secondary organic aerosols in the indoor environment are as presented in Table 4.

Table 4. Summary of some of the previous studies on SOA formation in indoor environment

Study	Location	Type of reaction	Sampling method	Microclimatic condition (Temperature RH and AER)
Coleman et al. [21]	a Teflon-lined, 198-L rectangular chamber	Ozone Initiated Reactions With Terpenes – Rich Household Products	SMPS coupled with OPC	23.0±0.5ºC; 3 h^{-1}AER
Langer et al. [22]	Two stainless steel reaction chambers (1 and 14 m^3)	ozone/limonene reactions in indoor air	SMPS coupled with CPC	23±2ºC; 33±3% RH
Angove et al.[25]	18.1m^3 CSIRO indoor environmental chamber	photodecomposition of 1,3-butadiene in air containing nitric oxide	Impactor jet connected to a condensation particle counter (CPC) and TSI 3030 electrical aerosol size analyser	21ºC; < 6% RH
Sarwar et al. [38]	11m^3 stainless steel chamber.	ozone–limonene reaction	A commercial corona discharge ozone generator (Living Air, BORA-IV) Particle Measuring Systems Inc., LASAIRs—	23ºC-25ºC; 39-67% RH

			Model 1002; TSI TM P-TRAK TM— Model 8525.	
Nøjgaard et al. [46]	1000 L Tedlar bags	ozonolysis of α-pinene and d-limonene	A differential mobility particle sizer (DMPS) and a CPC	21± 2ºC; RH < 1%
Lee et al. [47]	Carnegie Mellon University smog chamber,a 12m^{3}Teflon reactor and thermodenuder (TD)	Ozonolysis of monoterpenes	aerosol mass spectrometer (AMS) + CPC	70-90ºC;
Huang et al. [53]	18.26 m3 stainless-steel environmental chamber	Ozonolysis of pollutants from cleaning products	a scanning mobility particle sizer (SMPS) systemwith a differential mobility analyzer coupled to CPC	ACH of 0.36 h^{-1}, RH of 50% and T of 23ºC.
Chen and Hopke [55]	Dynamic chamber (2.5 m^3)	linalool ozonolysis	Scanning Mobility Particle Sizer (SMPS) coupled with Condensation Particle Counter(CPC)	(22–23ºC); 0.67±0.01 h^{-1} AER;
Kleindienst et al. [65]	The reaction Chamber is a14.5-m^3 parallelpiped, stainless-steel chamber with interior walls fused with a 40µm TFE Teflon coating.	isoprene + OH reaction in the absence of NOx	SMPS and Volatility Differential Mobility Analysis technique.	50-250ºC
Cao and Jang [68]	2m^3 indoor Teflon film chamber	Toluene photooxidation under various NOx conditions	SMPS and CPC	22-32ºC; 15-115% RH
Ng et al. [70]	Environmental	Photooxidation of	SMPS and	25ºC; < 6%

	chamber	terpenes	CPC	RH
Huang et al. [76]	100 L small scale chamber	Ozone initiated SOA emissions from painted wooden panels	NA	25ºC; RH of 50%; ACH of 0-0.5 h-1;
Matsunaga et al. [85]	A 5900 Litre PTFE environmental chamber	OH-radical initiated reactions of linear alkenes in the presence of NO_x	Thermal desorption particle beam mass spectrometer (TDPBMS)	<1% RH; at 25ºC;
Vivanco et al. [86]	EUPHORE photoreactor	Mixture of 1,3,5-trimethylbenzene, o-xylene, octane and toluene) with an oxidant .	TEOM and SMPS	10-20% RH;
Hatfield and Hartz [87]	5.5 m^3 Teflon smog chamber (Welch Fluorocarbon)	Mixtures containing reactive and non-reactive volatile organic compounds (VOCs)	ATSI SMPS coupled with CPC	23-29ºC; 1-4% RH
Parikh et al. [88]	Outdoor aerosol smog chamber	toluene oxidation	SMPS coupled with CPC	15–37ºC; 8-92%RH;
Song et al. [89]	Environmental chamber	Dark ozonolysis of ozonolysis of α-pinene	-	28ºC; 10% RH
Shilling et al. [90]	Environmental chamber	Dark ozonolysis	-	25ºC; 40% RH
Presto and Donahue [91]	Environmental chamber	UV	-	23ºC; <10%
Lauraguais et al. [92]	8 m^3 evacuable Plexiglas (PolyMethyl Methacrylatee PPMA) reaction chamber	gas-phase reaction of hydroxyl radical with syrindol (2,6-dimethoxyphenol)	(SMPS GRIMM, CPC5.404)	21-23ºC; 2 - 4% RH.
Updyke et al. [93]	a 17 L glass flow tube reactor	Photo-oxidation of VOCs from biogenic and anthropogenic sources	SMPS	20-24ºC; <2% (RH), and 750±50 mbar pressure
Stewart et al. [94]	80L collapsibleTeflon Static reaction chamber	Gas phase reactions of selected monoterpenes and cyclo-alkenes with ozone and NO_3 radical		25-27ºC;

Alfarra et al. [95]	27m^3 transparent Teflon® bag	Photooxidation of anthropogenic and biogenic precursors	Aerodyne Aerosol Mass Spectrometer (AMS), SMPS and CPC.	-
Broske et al. [96]	Aerosol flow tubes	reactions of O$_3$ with α-pinene, limonene or catechol and OH radicals with toluene or limonene.	SMPS-system (TSI 3071 electrostatic classifier and TSI 3022A condensation particle counter).	25ºC; 50- 57% RH
Carter et al. [97]	two collapsible 90 m^3 FEP Teflon film reactors	photolysis reactions of NO x and formaldehyde	SMPS coupled with CPC and tandem differential mobility analyzer (TDMA)	5-45ºC; unhumidified air
Chen and Chang [98]	2m^3 indoor Teflon film chamber equipped with UV- Visible lamps	Photooxidation of a mixture of dimethy sulfide and isoprene	Scanning Mobility Particle Sizer (SMPS) combined with a condensation nuclei counter (CNC).	21-24ºC; 12-80% RH
Cocker III et al. [99]	dual 28 m^3 Teflon reactor.	a-pinene/ozone system	Scanning electrical mobility spectrometers (SEMS), equipped with condensation particle counter	20-50ºC; <2 - 89% RH
Irei et al. [100]	8m^3 indoor YorkU smog chamber	Photooxidation of toluene	SMPS	25 ºC; andRH< 6%
Lee et al. [101]	Two suspended 28m^3 Flexible Teflon chambers	The ozonolyses of six monoterpenes (a-pinene,b-pinene, 3-carene, terpinolene, a-terpinene, and myrcene), two sesquiterpenes (a-humulene andb-caryophyllene), and	SOA yield was calculated theoretically	20 ± 1ºC; and <10% RH

		two oxygenated terpenes (methyl chavicol and linalool)		
Qi et al. [102]	Dual 90m^3 Teflon reactors	m-xylene photooxidation	Aerosol Particle Mass Analyzer (APM), Scanning Mobility Particle Sizers (SMPS) and a custom-built Hygroscopic Tandem Differential Mobility Analyzer (HTDMA).	0-40ºC;
Rickard et al. [103]	27m^3 Teflon bag	1,3,5-trimethylbenzene photooxidation	Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS), Condensation Particle Counters (CPCs) and a Scanning Mobility Particle Sizer (SMPS)	20ºC; 48-62% RH;
Rossignol et al. [104]	4.2m^3 stainless steel chamber in 200m^3 Euphore Photoreactor	limonene ozonolysis	Gravimetric analysis using 47mm quartz fibre filter	23ºC; 0 – 80% RH;
Salo et al. [105]	The AIDA chamber consists of an aluminium vessel of 84.5m^3	ozonolysis of tetramethylethylene (TME)	AIDA and SAPHIR	-90ºC-60ºC; 0.01-1000hPa
Na et al. [106]	18m^3 Teflon environmental chamber	Reaction of styrene with ozone in the presence and absence of ammonia and water	Scanning Electrical Mobility Spectrometer (SEMS) with differential mobility	20± 1 ^{o}C; 0 – 56% RH

			analyzer (DMA)	
Lu et al. [107]	The cuboid reactor, with a volume of $2m^3$	m-xylene/NOx photooxidation system	SMPS; SOA yield theoretically calculated according to Pankow (1994)	10-60ºC; RH < 20%
Sarwar et al. [108]	$11m^3$ stainless steel chamber.	homogeneous reactions between ozone anda-pinene,	A commercial corona discharge ozone generator (Living Air, BORA-IV) Particle Measuring Systems Inc., LASAIRs—Model 1002; TSI TM P-TRAK TM—Model 8525.	24ºC -33ºC;
Sarwar et al. [109]	$11m^3$ stainless steel chamber.	homogeneous reactions between O^3 and terpenes	A commercial corona discharge ozone generator (Living Air, BORA-IV) Particle Measuring Systems Inc., LASAIRs—Model 1002; TSI TM P-TRAK TM—Model 8525.	23ºC-25ºC;
Sleimann et al. [110]	an 18-m^3 environmental chamber	Ozone initiated reactions with nicitine and secondhand tobacco smoke	SMPS that consisted of electrostatic classifier coupled to an ultrafine CPC	25-150ºC; 0-50% RH
Fadeyi et al. [111]	236 m^3 field environmental chamber (FEC)	ozone of outdoor origin reacting with limonene of indoor	Fast Mobility Particle Sizer (FMPS)	23ºC; 1-2 h^{-1} AER

		origin.		
Huang et al. [112]	aromatherapy spa	Aromatic and volatile organic compounds were the dominant handling materials.	SMPS coupled with CPC	0.9-1.3 h^{-1} AER

2.2.1 Factors affecting secondary organic aerosol formation

Aside the reactive oxidizing agents, atmospheric conditions are factors that may influence the physical and chemical composition of SOAs [78]. Concentration of the reactive groups and terpenes have been acknowledged to have influence on growth and number concentration of SOAs [22,55]. Other factors that are affect SOAs formation discussed in the subsections below.

2.2.1.1 Light

Ozonolysis proceeds faster in the presence of illumination than in darkness. Oxidation of terpenes are mostly described to occur in the presence of light [77,78,79,80,81]. However, the investigation of Cao and Jang [66] and Presto et al. [69] showed that the presence of UV radiation has a negative effect on the ozonolysis of terpenes, especially α- pinene.Though, it is enhances the photolysis of H_2O_2 to OH radicals [80]. The investigations of Leungsakul et al. [81,82] on limonene/ozone reaction in a film chamber in both the presence of light and darkness indicated that SOA are formed in both cases.

2.2.1.2 Temperature

Ambient temperature has been found to have clear effect on the formation of secondary organic aerosols in terms of particle volume and chemical composition [83,84]. It has been established that SOAs formation is temperature dependent. The studies indicated that increase in temperature is directly proportional to secondary organic aerosols formation [83,84]. Studies have also established that ozonolysis of terpenes can occur at room temperature [85,86,87,90,91].

2.2.1.3 Relative humidity (RH)

RH affects the formation, size and deposition of SOAs [92]. The absorption of water by aerosols affects their physicochemical properties such as particle size [93], phase, deposition [94], atmospheric life time and chemical reactivity [80]. The hygroscopicity of aerosols depends on their chemical compositions [80]. Na et al. [106] have established that the presence of water vapour may inhibit the the formation of SOAs. The concentration of SOAs may depend on the water composition and distribution of the final oxidation products [113,114,115,116]. Under high humidity condition, SOAs adsorb water from the atmosphere and thus inhibit the reaction surface [95]. In contrast, investigation of the effect of RH on the formation of SOAs generated from ozonolysis of limonene in an environmental chamber by [106,107] indicated that the number concentration and growth of SOAs were enhanced as RH increases.

2.2.1.4 Air exchange rate (AER)

Air exchange rate is an important factor that determines the concentration of ozone indoor which has a typical half life of between 7 to 10 minutes [38]. Sarwar et al. [38] found out in their experiments that increase in air exchange rate increases the concentration of hydroxyl radicals in the indoor environment with alkene/ ozone reactions dominating. Weschler and Shields [97] studied the effect of air exchange rate on SOAs in indoor air. They observed that at higher AER, the mass and number concentrations of particles were smaller and no excess particle formation was detected. Previous studieshave indicated that lower air exchange rates will favour accretion and coagulation of smaller particles and that at higher air exchange rate, the small sized particles are likely to be formed within a short period [117,118,119,120].

2.2.1.5 Time

The residence time of air in the indoor environment is a factor that affects the growth of aerosol particle (accretion) and coagulation processes [121]. The more the time, the higher the concentration of airborne SOAs formed. High residence time and low air exchange rates are factors that may account for and increment in SOAs particle mass [122]. SOAs will continue to be formed in the indoor environment due to consumer product usage in as much as there are terpenes and the reactive group are in the indoor atmosphere. Waring et al. [122] noted that nucleation of particles will commence immediately terpenes are introduced into the indoor environment and that the time of reaction is almost inconclusive as new particles may be formed. Table 3 highlights the lifetime of reaction of some common terpenes, their reaction rate and OH⁻ formation as adapted from Fick [123].

Lifetime in Table 5 indicates time for decay of compound (terpenes) (37%) of its initial concentration at an ozone concentration of 28 ppb. Unit M is the molar yield of OH⁻.

Table 5. Reaction rate, lifetime and OH⁻formation from ozonolysis of common terpenes

Monoterpenes	Reaction rate 10^{18} x k (at 298 k) (cm^3 molecule^{-1} s^{-1})	Lifetime	OH radical formation (M)
α-pinene	86.6	4.6 h	0.85
β-pinene	15	1.1 day	0.35
Limonene	200	2h	0.86
Δ^3-carene	37	11h	1.06
Δ^2-carene	230	1.8h	No reported value
Myrcene	470	50min	1.15
Terpinolene	1880	12 min	1.03
Camphene	0.9	18 days	< 0.18
Sabinene	86	4.6 h	0.26
β-Phellandrene	47	8.0h	0.14

Source: Fick [123]

2.2.2 Mechanisms of SOA formation

Gas – particle partition stage is the second stage that will follow the oxidation of VOCs in the formation of SOAs [124,125]. Active ingredients in consumer product will react with the

reactive species in the gas phase followed by formation of new particles through coagulation, nucleation or accretion. SOAs are formed due to gas to particle conversion [126].

2.2.2.1 Gas phase reaction

Volatile components of consumer household spraying products (propellants and the active ingredients) enter the gas phase during and after use [41]. The gas phase reaction between terpenes and the reactive species such as O_3, OH^- radical and NO_x will lead to the formation of lower vapour pressure products [103]. Investigations have shown that the gas phase reaction between terpenes and ozone contributes significantly to the growth of SOAs in the indoor atmosphere [68,95,104,105,106,107] as ozone is usually removed in the indoor air as a result of the gas phase reaction [108].

2.2.2.2 Particle phase reaction

Gas/ Particle phase partitioning is a major phenomenon in SOA mass formation and occurs throughout the reaction time [97]. Low volatile oxidation products from gas phase reaction yield secondary organic aerosols either by new particle formation [127,128], or through condensation and nucleation of the already existing particles [81,82,129]. The nucleation and growth of aerosol particles can occur anywhere in the atmosphere [130,131] and most occurs at the beginning of ozone/ terpene reaction [45,97]. They are presumed to be responsible for the number concentration of SOAs that will be formed [132]. A major product of the particle phase reaction between ozone and terpenes is formaldehyde [133]. According to European Commission [61], gas to particle conversion has two perspectives including (i) a sink mechanism where reactive carbon is lost from the indoor atmosphere and (ii) the accretion of oxygenated material onto existing particle. These are summarized in Fig. 2. Gas–particle partitioning of products is usually calculated using the theory of Pankow which assumes that particulate organic matter (POM) is a single, liquid organic phase [33,35,85].

2.2.3 Impacts of SOAs on human health

Epidemiological studies have revealed that increase in exposure to aerosols is directly proportional to morbidity and mortality rates [134,135] and SOAs are believed to have more alarming effect on human health than the primary organic aerosols [77,136]. They have been associated with respiratory ailments [137,138] such as Asthma [139], cardiovascular health effects [106,140,141] and psychological stress [142]. They have also been noted for inflicting upper airway and pulmonary ailments on individuals [143]. Headaches, fatigue, eye, nose and throat irritation are also among the list of health impacts SOAs may have on humans [144].

2.2.4 Impact of SOAs on indoor environment

Secondary organic pollutants may be airborne for a long period of time. Singer et al. [30] noticed in a study that ozone consumption and OH radical persisted in the indoor air for about 10 – 12 hours following a brief cleaning exercise. SOAs may also be deposited on walls, and filters of the ventilation system [38]. Weschler [43] established that SOAs may be responsible for soiling of walls. In same experiments, it was noticed that the white board in the ozone/ limonene office turned slightly yellow due to SOAs deposition.
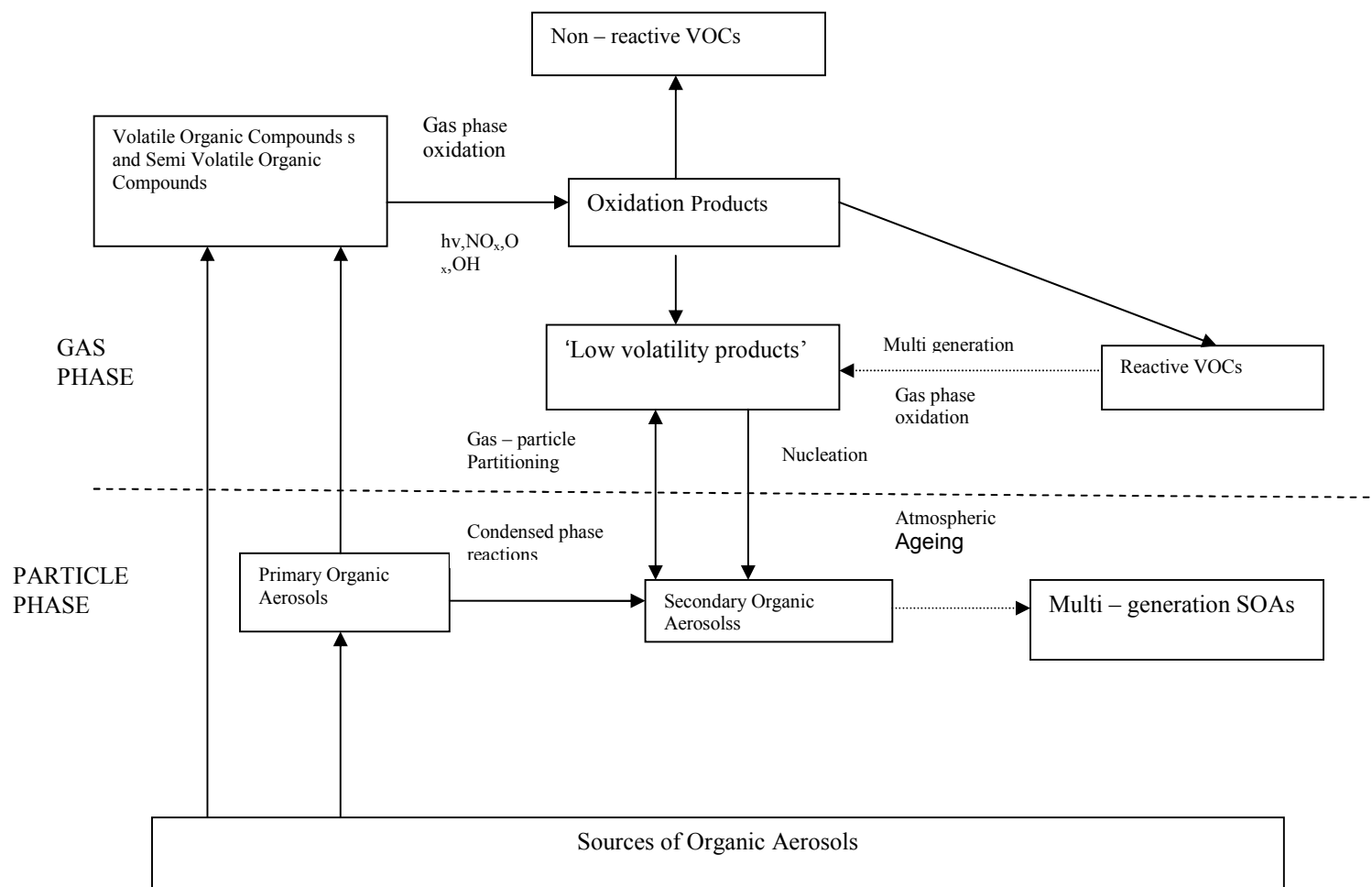
Fig. 2. Route of formation of secondary organic aerosols
Source: Wang [10]

3. MITIGATION MEASURES

Exposure to Secondary Organic aerosols from the use of consumer products can be reduced by removing ozone from ventilation air and limiting the use of terpenes emitting products. Proper and constant hygienic measures should be taken to replace the use of fragranced products. The use of room air cleaners has also been proved to be an effective means to improve indoor air quality [145,146]. Fadeyi et al. [111] suggested that high efficiency particulate filters could also be used to remove SOAs and ultrafine particles. The use of household and office electrical equipment that produce ozone should be minimized. Good ventilation and well-designed HVAC (Heating, Ventilation and Cooling) system should be given a top priority when designing a building. Regulation and legislation on manufacturing and declaration of contents in household products should be enforced as some contents are not often disclosed [147,148,149,150,151]. Bernstein et al. [150] opined that people should be informed about the existing air quality standards and rational environmental control.

4. CONCLUSION

The use of household spraying products may result in the increase in concentration of VOCs especially terpenes in the indoor environment. Terpenes react with the reactive radicals such as O_3, OH^- and NO_x in the presence/ absence of light to form SOAs which are presumed to have more adverse health effects on humans than the terpenes themselves. It is therefore recommended that a sensational measure should be put in place to educate consumers on the use of household spraying products. Legislations should be made in such a way that ingredients used in manufacturing these products will be fully declared. Efforts should be made to develop products that will have a drastically reduced VOCs.

5. RESEARCH GAPS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Qualitative estimate of the exact quantity of SOAs produced as a result of household products use has not been fully addressed in the literature. The available methods and techniques for quantifying SOAs may be insufficient to account for it. There is need to develop an approximate technique / equipment that will determine the approximate amount of SOAs yield. Uncertainties still arise as regards the effects of some factors affecting SOAs yield. Such uncertainties should be subjects of future research work. Formation of SOAs for consumer products should be considered as a critical area for further research work as little work found in the literature addressed this at present. Determination of undisclosed and unregulated VOC content recently researched into in some advanced countries (Steinemann [148;149] and Dodson et al. [151] should also be adopted by researchers and the regulatory agencies in the under-developed nations of the world.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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