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Atmospheric Reactions of Volatile Organics in The Optoelectronics Industry

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ABSTRACT

Possible VOC product species caused by atmospheric reactions were deduced in this study based on emission substances common in the optoelectronics industry; corresponding toxicological characteristics were subsequently investigated to determine the impact of prolonged inhalation in the external vicinity of optoelectronics factories. After an examination of the manufacturing processes of the optoelectronics industry, substances such as acetone, butanone, propylene glycol methyl ether acetate, dimethylsulfoxide, and N-methyl-2-pyrrolidone were selected for deduction. The results indicated four substances that were carcinogenic to the human body and six products that exceeded the Group 2 carcinogenicity classification of the International Agency for Research on Cancer; the toxicological data showed that most of the cancers targeted the organs of the liver, kidneys, and lungs.

KEYWORDS   Optoelectronics industry; Volatile organic compound (VOC);Carcinogenicity.

INTRODUCTION

The optoelectronics industry was listed as one of the target industries in the "Two Trillion, Twin Star" project of Taiwan in the 1990s. Despite the recent impact of international competition, a financial crisis, and industrial out-migration, the optoelectronics industry wanes in the twenty-first century. However, the optoelectronics industry remains a crucial industry in Taiwan. Nevertheless, the optoelectronics process uses many highly contaminating substances [1]such as volatile organic compounds (VOC), strong acids, and strong bases, which cause major concern regarding the effect of various gaseous, liquid, and solid environmental pollutants produced by the optoelectronics industry on environmental loading. Organic solvents such as photoresists, alignment solutions, and cleaning agents are used in the optoelectronics process. The specific

substances contained in the associated VOC emissions are difficult to identify because of frequent replacements of factory raw materials and business trade secrets. Moreover, people have limited knowledge regarding the environmental impacts of the optoelectronics processes, which involve chemical reactions through the mechanisms of the atmospheric dispersion of organic solvents, in-plant applications of strong acids (i.e., hydrochloric acid, hydrofluoric acid, and hydrocyanic acid), reactions within heating equipment (i.e., furnaces or regenerative incinerators), and atmospheric photochemical reactions that produce extremely toxic trace substances[2]. In this study, the organic emissions of the optoelectronics industry were analyzed to deduce the atmospheric reactions and the subsequent native and derivative organic pollutants emitted by the optoelectronics industry; from these data, the hazards of these toxicities on the human body were inferred.

Objective

The air pollution caused by VOCs has been extensively studied mainly because most organic substances cause noticeable odors and human sensory impacts such as nausea, drowsiness, and olfactory and emotional impacts. Subsequently, substantial amounts of data from monitoring the environment have shown that increasing ozone concentrations have been generated on the earth's surface. Repeated verifications have indicated that ozone primarily comprises the derivatives produced by VOCs through photochemical reactions. Therefore, studies have diverted from focusing on the environmental impacts of VOCs to various photochemical reactions, which involve the environmental hazards of photochemical smog in addition to ozone formation. VOC-related studies have gradually shifted toward the hazards of individual substances; numerous studies have focused on the individual components, in addition to determining total concentrations to investigate their carcinogenicity, noncarcinogenic health risks, and odors. Therefore, this study emphasized the VOCs emitted by the optoelectronics industry and deduced their atmospheric reactions to determine the health hazards.

LITERATURE REVIEW

The Optoelectronics Process

Generally, the optoelectronics industry refers to industries involving thin-film-transistor liquid-crystal displays (TFT LCDs), light emitting diodes, epitaxy, and solar energy. Among these products, the optoelectronics processes used in the production of TFT LCDs emit the largest quantity of VOCs and therefore receive the widest attention. Consequently, this study focused on the VOCs emitted during the TFT LCD manufacturing process.

Volatile Organic Compounds Emitted by Optoelectronics Plants

The aforementioned optoelectronics manufacturing processes involve numerous cleaning and coating procedures and thus use many cleaning and coating solutions. The types of cleaning agent and their purposes vary according to the different processes. According to statistics on raw materials used in the optoelectronics industry, the cleaning solutions comprise acidic, basic, organic, and inorganic solutions. Regarding organic cleaning solutions, the contents primarily include methanol, acetone, propylene glycol methyl ether (PGME), and propylene glycol methyl ether acetate (PGMEA). The

common organic solutions are shown in Table 1 [3].

According to investigative results by the Central Taiwan Science Park Bureau regarding air pollutants emitted by the semiconductor and optoelectronics industries (Table 1), air-polluting emissions of TFT LCD manufacturing processes in the optoelectronics industry can be typically divided into inorganic toxic waste gases, VOCs, basic gases, and acidic gases. Among these, VOCs are primarily used in self-assembled coatings and substrate cleaning procedures[1]; the emission substances comprise ethanol, acetone, benzene, toluene, ethylbenzene, xylene, styrene, cyclohexanone, isopropanol, PGME, PGMEA, hexamethyldisiloxane, trimethylfluorosilane, methyl methacrylate, trimethylethoxysilane, 2,4-dimethylhexane, 3-ethylhexane, 1,2,4-trimethylbenzene, and n-heptane.

Quantitative Structure–Activity Relationship

Quantitative structure–activity relationship (QSAR) is a method that uses molecular physical and chemical properties or structural parameters to investigate the interactions between organic micromolecules and biomacromolecules through mathematical and statistical quantitative means, which include

determining the physiological properties of absorption, distribution, metabolism, and excretion. QSAR is also commonly applied to assessing the toxicity of organic substances; a common equation for determining toxicities [4] is shown as follows:

$$\log(1/x) = \text{constant} + a_1 p_1 + a_2 p_2 + \ldots + a_n p_n \quad (1)$$

In toxicological calculations, x denotes the biotoxicological description; p_1–p_n denote the various bioreaction parameters (i.e., relevant material parameters such as lethal concentration 50; LC50); and a_1–a_n represent the corresponding constants. Therefore, the calculated results of the biotoxicological characteristics can be regarded as material property equations. QSAR is a method for determining preliminary toxicological characteristics for unknown substances given the molecular properties.

METHODS
Atmospheric Reaction Mechanisms of Organic Substances
Photochemical Reactions

The environmental impacts of VOCs are primarily caused by derivatives (or

secondary products) produced through airborne chemical reactions rather than by directly emitted substances.

In this study, the mechanisms of airborne photochemical reactions were derived to obtain the potential secondary pollutants based on the common free radicals and reaction formulae.

(a) Photochemical Reactions

Photochemical reactions initiate airborne chemical reactions; the reaction mechanisms of the airborne atoms, molecules, free radicals, or ions are initiated by illumination through the following general formula:

$$A + h\nu \longrightarrow A^* \qquad (2)$$

In the equation, A^* represents the excited state of Substance A; $h\nu$ is defined as the photon energy. Optical illumination results in the excited state A^*, which may proceed to the following reactions:

decompositon:

$$A^* \longrightarrow B_1 + B_2 \cdot \qquad (3)$$

direct reaction:

$$A^* + B \longrightarrow C_1 + C_2 \cdot \qquad (4)$$
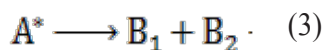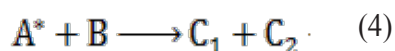
fluorescent reaction:

$$A^* \longrightarrow A - \qquad (5)$$

deactivation:

$$A^* + M \longrightarrow A \qquad (6)$$

In the aforementioned reactions, decomposition and direction reactions alter chemical properties; by contrast, the reaction products return to normal states after fluorescent and deactivation reactions. Among the photochemical reactions, decomposition reactions exert the greatest effect on successive reaction mechanisms, in which the other potentially formed free radicals or substances of varying chemical properties may also cause chain reaction mechanisms. Table 2 shows a compilation of the crucial photochemical decomposition mechanisms[5]. The common reactants in the troposphere were NO_2, O_3, and HNO_2; the product free radicals were also used for deriving the subsequent reaction formulae[6]

Reactions of Airborne Free Radicals

The most crucial objective when investigating the reactions of airborne organic substances is to determine the types of free radical produced. As discussed, airborne free radicals are primarily generated through photochemical reactions; however, the types of free radical generated are irrelevant to the subsequent reactions of organic substances.

(a) *Oxygen Atoms*

Oxygen atoms are primarily produced from ozone. The recurring reactions between oxygen atoms, oxygen gas, and ozone construct the primary mechanism for forming the ozonosphere. However, in the stratosphere, oxygen atoms may form from nitrogen oxides in addition to ozone; the formation reactions are shown as follows:

$$O_3 + h\nu \longrightarrow O + O_2 \qquad (7)$$

$$NO_2 + h\nu \longrightarrow NO + O \qquad (8)$$
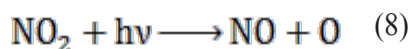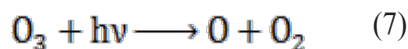
Highly active oxygen atoms and organic substances are relatively uncommon because oxygen atoms are extremely active. Therefore, contact between oxygen atoms and trace airborne organic substances is unlikely. However, oxygen atoms may still influence the activity of several compounds.

(b) *Hydroxyls*

Collisions between oxygen atoms and airborne water molecules potentially forms hydroxyls:

$$O + H_2O \longrightarrow 2OH\cdot \qquad (9)$$
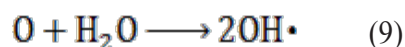
The presence of hydroxyls is crucial for determining the reaction mechanisms of airborne organic substances because hydroxyls exhibit relatively low activities toward oxygen. Consequently, hydroxyls are likely to react with trace airborne substances such as hydrocarbons or carbon monoxides. In this study, various reactions involving hydroxyls were indicated when deriving the reactions of airborne organic substances.

(c) *Halogens*

During etching and pickling procedures in the optoelectronics

industry, substantial amounts of strong acids, namely hydrochloric acid, hydrofluoric acid, and hydrobromic acid, are used as cleaning agents. Strong acids tend to form highly active halogens, such as Cl·, F·, and Br·, which share similar mechanisms with the reaction mechanisms of chlorofluorocarbons (substances that damage the ozone). However, in the presence of complex organic substances, these halogens are extremely likely to react with VOCs and alter their chemical properties or even produce toxic substances. The following formula uses the example of hydrochloric acid to express the halogen-forming mechanism:

$$OH\cdot + HCl \longrightarrow H_2O + Cl\cdot \qquad (10)$$
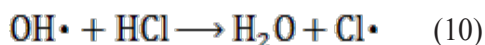
Reactant Analysis

The optoelectronics industry produces an assortment of VOCs. Optoelectronics plants use different organic solvents for the production of various products. However, based on known test results, the most common organic substances are methanol, toluene, acetone, butanone, PGMEA, PGME, DMSO, and N-methyl-2-pyrrolidone

(NMP). Among these, methanol exhibits the simplest chemical structure and reacts similarly to ketones; hence, the reactions of acetone and butanone were discussed, whereas that of methanol was excluded. Additionally, the chemical formula of PGMEA is extremely similar to that of PGME, therefore the reaction products of PGMEA (consists of an additional functional group) and PGME were similar when the reactions were derived. Aromatic chemicals are extremely stable substances; therefore, the airborne reaction mechanisms of toluene are scarce because the ring structures cannot be easily attacked through photochemical reactions. Consequently, the airborne reaction mechanisms also excluded the possible reaction of toluene. In summary, this study focused on the airborne reactions of acetone, butanone, PGMEA, DMSO, and NMP to deduce the substances produced.

Deduction of Toxicological Characteristics

Through the deduction of chemical reaction formulae, most of the deduced products yielded unknown species. The deduction of product toxicological characteristics involved adopting the QSAR model. The Toxicity Estimation Software Tool (TEST) model, developed by the US Environmental Protection Agency (EPA) was applied in this study. The TEST model

enables inputting chemical structures and using the built-in QSAR program to deduce the toxicological characteristics.

The 96-h LC50 (Endpoint 1) and teratogenicity (Endpoint 7) of the killifish were adopted to investigate the toxicological characteristics for each chemical species.

RESULTS AND DISCUSSION
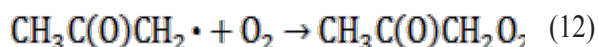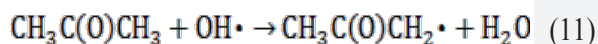### Airborne Reactions of Volatile Organic Compounds

The optoelectronics industry emits a wide variety of VOCs; various pollutants are produced from different production lines. Pollution derivatives were investigated according to annual statistics on the most commonly emitted (discharged) pollutants from the optoelectronics industry. The investigation involved deducing the atmospheric reactions of the organic substances of acetone, butanone, PGME, PGMEA, DMSO, and NMP.
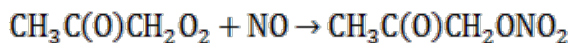
Acetone and Butanone

The chemical formulae of acetone and butanone are $CH_3C(O)CH_3$ and $CH_3C(O)CH_2CH_3$, respectively. The two chemicals are widely used as cleaning agents in the high-tech optoelectronics,
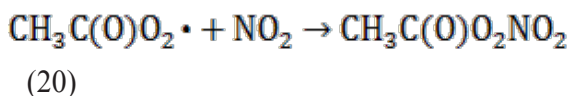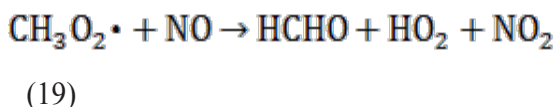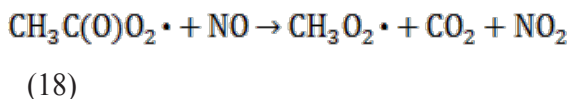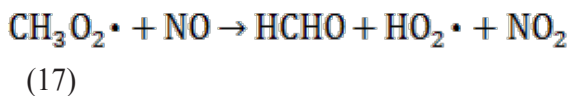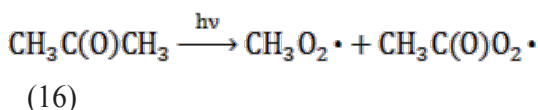
semiconductor, and printed circuit board industries for cleaning organic impurities on substrate surfaces and on various components in other cleaning procedures and are therefore common pollutants in high-tech industries. Ketones involve two types of atmospheric organic reaction mechanism: hydroxide free radical ($OH \cdot$) and solar-illuminated photochemical reactions. Acetone and butanone have long been used in various applications; therefore, their deduced relevant reaction formulae are comparatively complete in the literature. The following shows the derivation of the airborne reactions for acetone and butanone according to the relevant derivation formulae proposed by Atkinson and Lloyd in 1984.

After reacting with airborne hydroxide free radicals, acetone may subsequently react with airborne oxygen to form peroxy acids ($CH_3C(O)CH_2O_2$), which then react with airborne nitric oxide and possibly form $CH_3C(O)CH_2ONO_2$ and $CH_3C(O)CHO$ through the complete reaction formulae[7]shown as follows:

$$CH_3C(O)CH_3 + OH\cdot \rightarrow CH_3C(O)CH_2\cdot + H_2O \quad (11)$$

$$CH_3C(O)CH_2\cdot + O_2 \rightarrow CH_3C(O)CH_2O_2 \quad (12)$$

$$CH_3C(O)CH_2O_2 + NO \rightarrow CH_3C(O)CH_2ONO_2 \quad (13)$$

$$CH_3C(O)CH_2O_2 + NO \rightarrow CH_3C(O)CH_2O \cdot + NO_2 \quad (14)$$

$$CH_3C(O)CH_2O \cdot + O_2 \rightarrow CH_3C(O)CHO + HO_2 \cdot \quad (15)$$
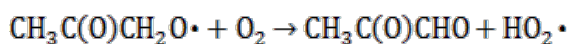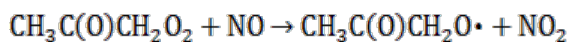
Regarding photochemical reactions, acetone decomposes into methane and acetaldehyde radicals and separately forms formaldehydes and peroxy acids through reacting with nitrogen oxide [8,9,10]. When compared to the aforementioned oxidation reactions, the products are relatively similar to the discussed airborne free radicals with the exception of a missing methyl (CH_3); this reaction occurs as follows:

$$CH_3C(O)CH_3 \xrightarrow{h\nu} CH_3O_2 \cdot + CH_3C(O)O_2 \cdot$$
(16)

$$CH_3O_2 \cdot + NO \rightarrow HCHO + HO_2 \cdot + NO_2$$
(17)

$$CH_3C(O)O_2 \cdot + NO \rightarrow CH_3O_2 \cdot + CO_2 + NO_2$$
(18)

$$CH_3O_2 \cdot + NO \rightarrow HCHO + HO_2 + NO_2$$
(19)

$$CH_3C(O)O_2 \cdot + NO_2 \rightarrow CH_3C(O)O_2NO_2$$
(20)

The product in (20) is peroxyacetyl nitrate (PAN), which is one of the main components of photochemical smog (e.g., in Los Angeles). The aforementioned reaction formulae show that the oxidation and photochemical reactions of acetone may produce the substances of

$CH_3C(O)CH_2ONO_2$ (peroxy acids),

$CH_3C(O)CHO$, $HCHO$ (formaldehyde),

and $CH_3C(O)O_2NO_2$ (PAN).
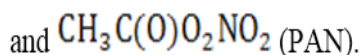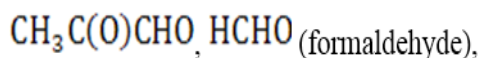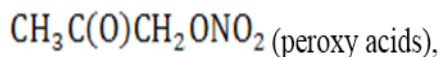
Because butanone and acetone are structurally similar, reactions similar to acetone were deduced according to the reactions of the aforementioned reaction formulae. Associated with an additional methyl group, the following species were the reaction products [11]:

$CH_3CH_2C(O)CH_2ONO_2$,

$CH_3CH_2C(O)CHO$, CH_3CHO

(acetaldehyde), and $CH_3CH_2C(O)O_2NO_2$.
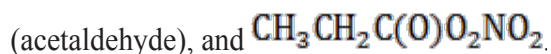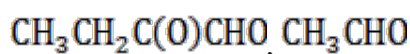
Propylene Glycol Methyl Ether Acetate
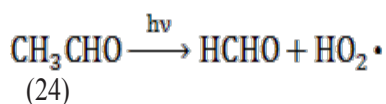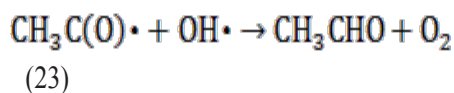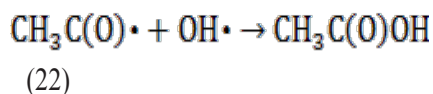
PGMEA is a common photoresist solvent used in optoelectronics processes and has a chemical formula of $CH_3C(O)OCH(CH_3)CH_2OCH_3$. This substance can be detected on the perimeter of numerous optoelectronics industrial plants, which indicates the wide acceptance

of PGMEA in the high-tech industry. The airborne reaction mechanisms of PGMEA lack reports in relevant studies. The following deduces airborne PGMEA products according to potential airborne reactions [12] .
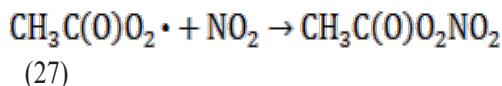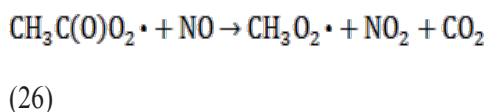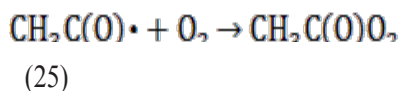
When reacted photochemically, the original PGMEA reacts into the two substances $CH_3C(O)$ and $COH(CH_3)CH_2OCH_3$ through the following chemical formula (21)

$$CH_3C(O)OCH(CH_3)CH_2OCH_3 \xrightarrow{h\nu} CH_3C(O)\cdot + CHO(CH_3)CH_2OCH_3$$
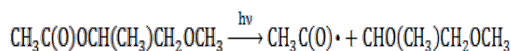
Among the species, $CH_3C(O)$ subsequently reacts photochemically to form substances such as acetic acid, acetaldehyde, and formaldehyde:
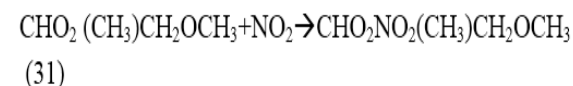
$$CH_3C(O)\cdot + OH\cdot \rightarrow CH_3C(O)OH$$
(22)

$$CH_3C(O)\cdot + OH\cdot \rightarrow CH_3CHO + O_2$$
(23)

$$CH_3CHO \xrightarrow{h\nu} HCHO + HO_2\cdot$$
(24)

In addition, $CH_3C(O)$ also reacts with oxygen gas to form the peroxide $CH_3C(O)O_2$, which combine to form $CH_3C(O)O_2NO_2$ through the following reaction mechanisms:

$$CH_3C(O)\cdot + O_2 \rightarrow CH_3C(O)O_2$$
(25)

$$CH_3C(O)O_2\cdot + NO \rightarrow CH_3O_2\cdot + NO_2 + CO_2$$
(26)

$$CH_3C(O)O_2\cdot + NO_2 \rightarrow CH_3C(O)O_2NO_2$$
(27)

Additionally, PGMEA reacts photochemically to form the substance $CHO(CH_3)CH_2OCH_3$, which reacts with hydroxyls to form $COOH(CH_3)CH_2OCH_3$ or isopropanoic acid methyl ether:

$$CHO(CH_3)CH_2OCH_3 + OH\cdot \rightarrow COOH(CH_3)CH_2OCH_3 + H\cdot$$
(28)
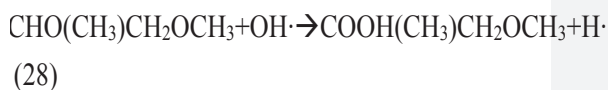
Identical to (27), the peroxide formed through the reaction with NO may subsequently produce PAN through the following reaction formulae:

$$CHO(CH_3)CH_2OCH_3\cdot + O_2 \rightarrow CHO_2(CH_3)CH_2OCH_3 + O\cdot$$
(29)

$$CHO_2(CH_3)CH_2OCH_3 + O_2 \rightarrow CHONO_2(CH_3)CH_2OCH_3$$
(30)

$$CHO_2(CH_3)CH_2OCH_3 + NO_2 \rightarrow CHO_2NO_2(CH_3)CH_2OCH_3$$
(31)
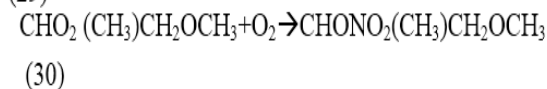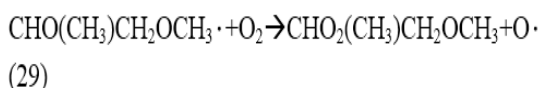
When $CHO(CH_3)CH_2OCH_3$ reacts photochemically, the formation of two free radicals through the removal of CH_3 may also

produce $CHO(CH_3)CH_2O$; the substance produced through this reaction can be relatively complex. The reaction with airborne NO may yield compounds such as $CHONO_2(CH_3)CH_2ONO_2$, $CHONO_2(CH_3)CH_2OH$, $CHOH(CH_3)CH_2ONO_2$, $COOH(CH_3)CH_2ONO_2$, and $CHONO_2(CH_3)COOH$. The following shows an example reaction of $CHONO_2(CH_3)CH_2ONO_2$:
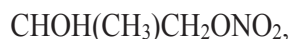
$$CHO(CH_3)CH_2OCH_3 \cdot \xrightarrow{h\nu} CHO(CH_3)CH_2O \cdot\cdot + CH_3 \cdot$$

(32)

$$CHO(CH_3)CH_2O \cdot\cdot + O_2 \rightarrow CHOO(CH_3)CH_2OO$$

(33)

$$CHOO(CH_3)CH_2OO + 2NO \rightarrow CHONO_2(CH_3)CH_2ONO_2$$

(34)

Substantial amounts of strong acids are used in the optoelectronics industry for cleaning and etching processes and are therefore likely to react with organic substances in the atmosphere. The acids are primarily hy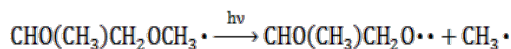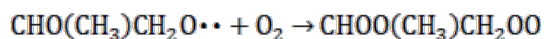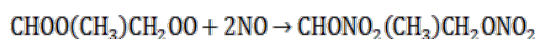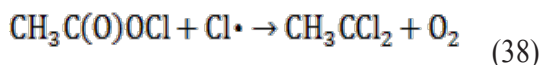drochloric, hydrofluoric, and hydrocyanic acids, which become ionized in the atmosphere through solar irradiation to form ions such as $Cl\cdot$, $F\cdot$, and $CN\cdot$. Among these, chloride ions become oxidized by oxygen gas to form hypochlorite ions ($ClO\cdot$

); these ions subsequently react with $CH_3C(O)$ to form products such as $CH_3C(O)Cl$, $CH_3C(O)OCl$, $CH_3C(OCl)_2$, and CH_3CCl_2 through the following reaction formulae[13] :

$$CH_3C(O)\cdot + Cl\cdot \rightarrow CH_3C(O)Cl$$

(35)

$$CH_3C(O)\cdot + ClO\cdot \rightarrow CH_3C(O)OCl$$

(36)

$$CH_3C(O)OCl + Cl\cdot \rightarrow CH_3C(OCl)_2$$

(37)

$$CH_3C(O)OCl + Cl\cdot \rightarrow CH_3CCl_2 + O_2$$

(38)
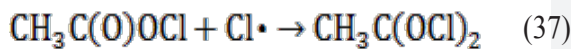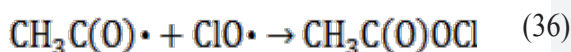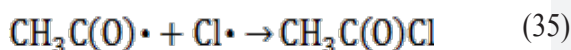
Additionally, $CHO(CH_3)CH_2OCH_3$ also reacts with chloride and hypochlorite ions. In summary, the reaction between the PGMEA derivative $CHO(CH_3)CH_2OCH_3$ and $CH_3C(O)$ can form the following substances:

(a) through reacting with $CHO(CH_3)CH_2OCH_3$: $CHOOCl(CH_3)CH_2OOCl$, $CHOCl(CH_3)CH_2OCl$, $C(O)OCl(CH_3)CH(O)OCl$, $C(OCl)_2(CH_3)CH(OCl)_2$, $CHCl(CH_3)CH_2Cl$, and $CCl_2(CH_3)CCl_3$

(b) through reacting with $CH_3C(O)$:

$CH_3C(O)Cl$, $C(O)Cl_2$, $CH_3C(O)OCl$, $C(O)(OCl)_2$, CH_3CCl_3, and $CH_3C(OCl)_3$

Additionally, hydrofluoric and hydrocyanic inorganic acids are often used in optoelectronics plants; these inorganic acids also tend to ionize in the atmosphere into ions such as fluoride ($F\cdot$) and cyanide ($CN\cdot$) ions through similar mechanisms to those of chlorde ions. The dediuced reaction products are compiled in Table3.

Dimethylsulfoxide

Dimethylsulfoxide (DMSO) has the chemical formula of $(CH_3)_2SO$; its use can be traced back to the Second World War. DMSO is an organic solvent that exhibits excellent solubility, which found early applications in paint thinners and solvents and is presently used as a cleaning solvent in the electronic industry; in the optoelectronics industry, DMSO is also used as a cleaning agent.

DMSO exhibits a simple chemical structure with presumed properties similar to that of sulfur dioxide and tends to oxidize to $(CH_3)_2SO_2$ through solar irradiation and oxygen contact. Additionally, DMSO tends to react with organic peroxides through the following mechanism:

$RCHOO+(CH_3)_2SO \rightarrow RCHO+(CH_3)_2SO_2$ (40)
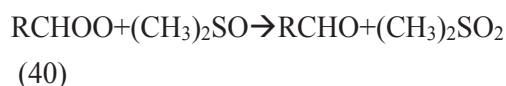
Peroxides may form aldehydes with DMSO, which closely resembles SO_2. Moreover, DMSO may react with airborne alcohols to form aldehydes or ketones through the Swern oxidation reaction, a crucial alcohol and ketone reaction. DMSO is required as a catalyst for the Swern reaction, although trifluoroacetic anhydride and trimethylamine are required as reaction intermediates. However, trimethylamine is also a crucial cleaning agent in the optoelectronics industry; therefore, the formation of aldehydes and ketones in the complex emission species of the optoelectronics industry cannot be ignored, with a possible reaction [13].

N-methyl-2-pyrrolidone

NMP is a compound that exhibits a cyclopentane base structure, which is vulnerable to thermal attack. The potential breakage site of the pentagonal carbon ring is located at the carbonyl–nitrogen bonds. Therefore, NMP structural compounds are mostly likely to decompose into $CO(CH_2)_3N(CH_3)$ through a process similar to the aforementioned reaction. After ring breakage, $COOH(CH_2)_3NO(CH_3)$ is formed through atmospheric oxidation, which also presents a process similar to that derived for

11

PGMEA. Subsequently, NMP forms peroxides such as $CONO_2(CH_2)_3NO(CH_3)$ and $CO_2NO_2(CH_2)_3NO(CH_3)$ or nitrate-based compounds such as $CONO_2(CH_2)_3NO_2$ and $CO_2NO_2(CH_2)_3NO_2$ when the N and CH_3 bonds are replaced by oxides.

Interactive Airborne Reactions

The discussed reactions show substances forming organic ethers, esters, acids, alcohols, and aldehydes[14] through the involvement of the following reactants: chlorides, fluorides, nitrogen oxides, sulfur oxides, oxygen anions, and hydroxyls. However, compounds are produced that enable interactions between different species: $CO(CH_2)_3N(CH_3)$ through the decomposition of cyclic NMP compounds and $CH_3C(O)C(O)(CH_2)_3N(CH_3)$ forms through a reaction with $CH_3C(O)$. Consequently, airborne chemical products are abundant. According to the structures of toxic chemicals and other toxic substances announced by the EPA and the possible optoelectronics plant emissions, the potential substances are provided in Table 4. For example, the aforementioned substances show that the ethers formed (i.e., from the reactions of PGMEA) can also subsequently

react with chloride ions to form bis-chloromethylether $(CH_2Cl)_2O$. Specifically, organic compounds may also form increasingly complex substances such as pesticidal ingredients. Because these ingredients are produced through complex chemical processes, the pesticide ingredients possibly produced in the atmosphere may exhibit negligible concentrations or extremely short formation periods; however, pesticides are extremely toxic and pose severe health hazards despite negligible concentration

Toxicological Characterization

Carcinogens

Eighteen of the VOC products deduced in this study belong to the toxic chemicals announced by the EPA; among these, four substances were proven human carcinogens: formaldehyde, bis-chloromethylether, 1,2-dibromo-3-chloropropane, and chloromethyl methyl ether. The carcinogenicity classification of the International Agency for Research on Cancer (IARC) comprises 11 types of substance; three substances deduced in the study were in Group 1 (i.e., proven human carcinogens), and six substances were in Group 2B (i.e., possible human carcinogens). The toxicology data showed

that the vulnerable organs included the liver, kidneys, and lungs.

Quantitative Structure–Activity Relationship

In addition to the listed IARC carcinogenicity classifications, the TEST model was adopted for the remaining substances to quantify the toxicological characteristics. The simulation endpoints adopted the killifish-96-h LC50 and teratogenicity tests to investigate the toxicological characteristics of each species. Furthermore, the simulation parameters of the classified substances were compared. However, because of the limitations of the TEST model functions, the NO_2-functional groups could not be simulated for each substance.

Through experimental simulation, CCl_4, $CCl_2(CH_3)CCl_3$, and $CH_2BrCHBrCH_2Cl$ exhibited LC50s (approximately 2–3{-Log10[mol/L]}) greater than 4. Structural equations showed that substances with comparatively high chlorine or bromine contents exhibited increased LC50s, which indicate high carcinogenicity. Regarding teratogenicity, the positive simulated substances comprised $CH_3C(OCl)_3$, $C(O)(OCl)_2$, $C(OCl)_4$, $C(OCl)_2(CH_3)CH(OCl)_2$, $(CH_2Cl)_2O$, and

$CH_2BrCHBrCH_2Cl$. Although the deduced teratogenicities of CH_2ClOCH_3 and $CH_2ClCOOH$ were positive, those experimentally obtained were negative. According to structural formulae, the substances with high oxygen and chloride contents exhibited an increased likelihood of teratogenicity, whereas teratogenicity and the known carcinogens exhibited comparatively high correlations.

CONCLUSION AND RECOMMENDATIONS

CONCLUSIONS

(a) Most of the deduced VOCs remained as peroxides; moreover, numerous compounds were ethers and esters.

(b) The derived substances comprised 20 known toxic compounds, of which four were proven carcinogens according to the EPA and nine were carcinogenic substances greater than the IARC Group 2 classification. The toxicology data showed that most of the carcinogens target the human liver and kidneys, followed by the central nervous system and respiratory system diseases.

(c) The QSAR TEST model simulation results showed that three substances exhibited high LC50s and that seven substances demonstrated teratogenicity. According to the QSAR simulation results, substance carcinogenicity can be related to chloride and bromide reactions, which indicates that organic substances are extremely likely to produce carcinogens following reacting with strong acids.

RECOMMENDATIONS

By deducing the reactions of organic substances in this study, several VOC substances emitted by the optoelectronics industry have been confirmed as human carcinogens. To verify the specific impact of these substances on public health, several topics are suggested for subsequent studies:

(a) Experimentally verify the deduced chemical reactions: Most of the deduced chemical reactions were theoretically derived without known reaction constants. Therefore, simulations such as smoke chamber experiments can be adopted to mimic the airborne reaction products of optoelectronics industrial emissions and verify the deduced chemical reaction formulae.

(b) Deduce chemical toxicities: A number of unknown substances were deduced as reactants; consequently, the corresponding toxicological characteristics are difficult to determine. Quantitative QSAR methods are recommended for describing the toxicity of the derived substances in subsequent studies.

Follow-up investigations are required because the cleaning agents and alignment solutions in optoelectronics processes that contain VOC solvents are continually being replaced. Therefore, identifying the replacement substances (i.e., the organic solvents) is necessary to subsequently determine potentially lethal organic reaction products.

ACKNOWLEDGMENTS

Table list
Table 1. Properties of organic solvents commonly used in the optoelectronics industry

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Solvent content	Chemical formula	Density (g/mL)	Boiling point (°C)	Permissible exposure limit (ppm)
Methanol	CH_3OH	0.792	64.5	200
Isopropanol	$(CH_3)_2CHOH$	0.786	82.4	400
Acetone	$(CH_3)_2CO$	0.791	56.2	750
PGMEA	$C_6H_{12}O_3$	0.957	146	200
PGME	$C_4H_{10}O_2$	0.915	120	100
Hexamethyldisilazane	$C_6H_{19}NSi_2$	0.772	399.2	—
Butyl acetate	$CH_3CO_2C_4H_9$	0.883	126	150
Dimethylsulfoxide (DMSO)	$(CH_3)_2SO$	1.095	189	—
Ethylmethylamine	$CH_3(CH_2)_2NH_2$	1.018	172	3
Butyldiglycol	$C_8H_{18}O_3$	0.904	231	—

Table 2. Photochemical reaction formulae

Substance	Reaction formula
NO_2	$NO_2 + h\nu \longrightarrow NO + O$
O_3	$O_3 + h\nu \longrightarrow O + O_2$
HNO_2	$HNO_2 + h\nu \longrightarrow NO + OH$
H_2O_2	$H_2O_2 + h\nu \longrightarrow 2OH$
NO_3	$NO_3 + h\nu \longrightarrow NO + O_2$ $\longrightarrow NO_2 + O$
$HCHO$	$HCHO + h\nu \longrightarrow HCO + H$ $\longrightarrow CO + H_2$
CH_3CHO	$CH_3CHO + h\nu \longrightarrow CH_3 + HCO$
$CH_3C(O)CH_3$	$CH_3C(O)CH_3 + h\nu \longrightarrow CH_3 + CH_3CO$
$CH_3CH_2C(O)CH_3$	$CH_3CH_2C(O)CH_3 + h\nu \longrightarrow C_2H_5 + CH_3CO$ $\longrightarrow CH_3 + C_2H_5OH$

Table 3. Reactions between PGMEA and hydrochloric, hydrofluoric, and hydrocyanic acids (1/2)

Airborne VOC substance	Reactant 1	Reactant 2	Reaction product	Name	Note
PGMEA	$CH_3C(O)$	HCl	$CH_3C(O)Cl$	Acetyl chloride	
			$CH_3C(OCl)_3$	Ethyl trihypochlorite	
			$CH_3C(O)OCl$	Acetyl hypochlorite	
			CH_3CCl_3	1,1,1-trichloroethane	
			CH_3CHCl_2	1,1-dichloroethane	
			CH_3CH_2Cl	Chloroethane	Class I toxic substance
			$C(O)(OCl)_2$	Dihypochlorite formaldehyde	
			$C(O)Cl_2$	Phosgene	Class I and III toxic substance
			$C(OCl)_4$	—	
			CCl_4	Carbon tetrachloride	Class I toxic substance
		HF	$CH_3C(O)F$	Acetyl fluoride	
			CH_3CF_3	1,1,1-trifluoroethane	
			CH_3CHF_2	1,1-difluoroethane	
			CH_3CH_2F	Fluoroethane	
			$C(O)F_2$	Difluoro formaldehyde	
			CF_4	Carbon tetrafluoride	
		HCN	$CH_3C(O)CN$	—	
			$CH_3C(CN)_3$	—	
			$CH_3CH(CN)_2$	—	
			CH_3CH_2CN	Propionitril	
			$C(O)(CN)_2$	—	
			$C(CN)_4$	—	

Table 4. Reaction products of toxic organic emission substances from the optoelectronics industry

Reaction product	Chemical formula	Possible source substance
Bis-chloromethylether	$(CH_2Cl)_2O$	PGMEA, HCl
1,2-dibromo-3-chloropropane	$CH_2BrCHBrCH_2Cl$	PGMEA, PGME, HCl
Methyl isocyanate	CH_3OCN	PGMEA, acetone, HCN
Chloroform	$CHCl_3$	Acetone, HCl
Chloromethyl methyl ether	CH_2ClOCH_3	PGMEA, HCl
1,1,2,2-tetrachloroethane	$CHCl_2CHCl_2$	PGMEA, HCl
Chloromethane (methyl chloride)	CH_3Cl	PGMEA, PGME, acetone, HCl
Dichloromethane (methylenechloride)	CH_2Cl_2	PGMEA, PGME, acetone, HCl
Chloroacetic acid	$CH_2ClCOOH$	PGMEA, acetic acid, acetone, butanone, HCl
Ethyl chloroformate	$ClCOOC_2H_5$	PGMEA, acetic acid, butanone, HCl
Acetonitrile	CH_3CN	PGMEA, PGME, HCN
Triethylamine	$C_6H_{15}N$	NMP
Chloroethane (ethyl chloride)	C_2H_5Cl	PGMEA, PGME, acetone, HCl

Figure Captions
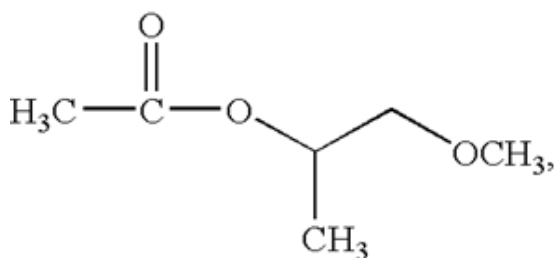
Fig 1. The structural formulae of Propylene Glycol Methyl Ether Acetate
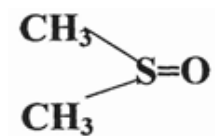
Fig 2. The structural formulae of Dimethylsulfoxide
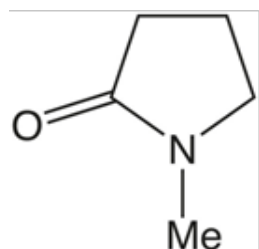
Fig 3. The structural formulae of N-methyl-2-pyrrolidone

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