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A Scientific Overview Of Emerging Pro-Fragrance Technologies And Its Applications In Product Development

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Introduction

The tradition of smell and perfumes has been related to the humans from time immemorial. Fragrances have become an indispensable article for us to relate with Fragrances comes in contact with us in throughout from the start of the day till we go to sleep. It could be in a form of simple shower gel that we use for getting bathing pleasure and feel fresh to Eau de toilet that we may apply to arouse senses and calming down before going to sleep. An important thing that we always desire from the fragrance is its ability to stay longer and give efficacious performance ever hours after application. An effective to increase the long lastingness of the fragrance is to use the Pro-fragrance technology in the perfume design. A perfume designer's pallet will have lot of fragrant raw materials to choose from. His ability to mix and match to create the most desired mix matching the concept and capable of triggering the user's emotion will be decided by the individual properties of the fragrance compounds. Of all the properties the most important is the volatility.

The Pro-fragrance technology makes it possible to play with the volatilities of these molecules. Primarily when a highly or moderately volatile molecule is chemically bonded with a low volatile molecule which could be fragrance molecule or other non-fragrance molecule. All the volatile molecules evaporate and reach their target by molecular diffusions. Since their molecular weights are low they have a low Olfactive threshold. It has been reported that to naturally release the biomolecules [1] found in nature such as biomolecules fragrances, pheromones and other signaling compounds, nature uses precursors such as the glycosides which are stored in the plant as complexes and are acted upon by the enzymatic mechanisms to liberate the volatile part. Hence inspired by a lot of natural precursors, researchers have developed pro-fragrance technologies especially in the functional perfumery [2] [3]. An essential condition for the pro-fragrance molecules to perform in the daily environmental conditions is its ability to undergo cleavage because of hydrolysis, oxidation due to contact with air, photo oxidation because of light, change in temperatures etc. The scheme is reported in the figure 1 [4] illustrates the concept of controlled release of the fragrance molecules.

Many attempts were made by the researchers to transfer the encapsulation technology from pharmaceutical industry to the fragrance industry as a medium for controlled release of the fragrance but it has limited applications considering the different volatilities of the fragrance molecule and different nature of substrates. It was reported by Dr. Andreas Herrmann et. al. [5] that there could be possible two class of interesting molecules which are namely those which are hydrolytically cleavable and light induced photo oxidative.

Hydrolytic cleavage

These kind of mechanism are applied by use of principle called the intramolecular catalysis. This can be explained by a peculiar example of the groups such as benzoates, maleates and succinates that can be modified chemically [6]. It was reported by Dr. Herrmann et al. that the said class of molecules, particularly the ortho substituted benzoates maleates and succinates help release of the fragrance alcohols by the intramolecular cyclization using a nucleophilic substitution group (X) that is generated in situ because of change in p(H). Depending on the acidic or basic conditions It was reported that the rates of hydrolysis are dependent upon the structure of the evaporating alcohols. Comparatively the esters of the primary alcohols evaporated faster than the higher order alcohols. It also depends upon the precursor skeleton and the disrupting nucleophilic moiety (FIG. 1). For the successful commercialization of the pro-fragrance technologies it is very important is the stability of the precursors during storage. There could be possibility that under the prevailing environmental conditions it is possible for the pro-fragrance molecule to undergo degradation. To avoid this, it was reported that it is possible to keep the precursor in the company of the trigger particularly in the case of water based personal care products like shower gel etc.

Recently it is possible by the use of covalent chemistry to create dynamic mixtures which are prone to reversibility where there is always a possibility to restore the molecule to its original form in spite of changing conditions. Dr. Herrmann et.al. studied the peculiar case of reversibility of the aminals and hydrazones as fragrance delivery systems in the aqueous solutions (FIG. 2). The addition of hydrazine or diamine derivative to a group of fragrance aldehydes and ketones in the presence of water can lead to the formation of dynamic mixtures which then can act as pro-fragrance trigger mechanisms. As the fragrance evaporates the rate of reaction is shifted backwards again leading to more regeneration of the hydrazine and diamine. This application is particularly useful in the formulation of fabric softeners and laundry detergents. This mechanism was reported to contribute to a long lasting effect on tested cotton cloths where the applied perfumes had a mixture of carbonyl compounds. A headspace analysis of this mixture has showed that the concentration of the fragrance molecules has increased significantly compared to reference without the diamine and hydrazine mixtures .

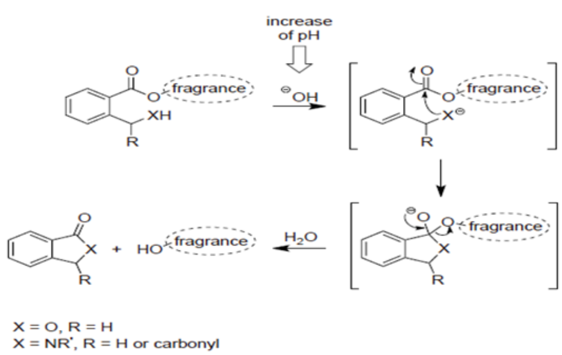

FIG. 1. **Controlled release of fragrance alcohols by niebhouring group participation of Ortho- substituted benzoate molecules.**

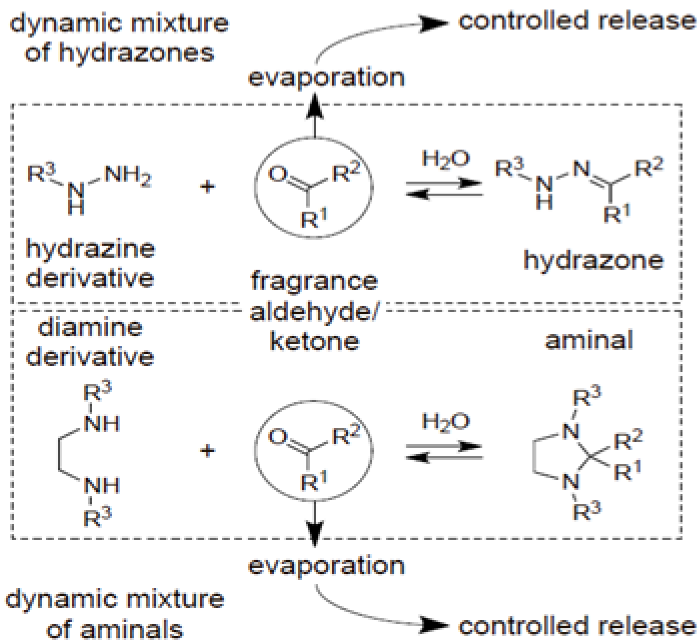

FIG. 2.**Concept of reversible formation of the hydrazones and aminals for controlled release of the fragrance aldehydes and ketones.**

Light induced pro-fragrance cleavage

It has been reported that fragrance evaporation takes place from surfaces could be because of sunlight. Hence photo responsive fragrance can be an ideal delivery system for the volatile compounds The photo reactive delivery system may be based upon certain certain molecules which in presence of oxygen and low intensity light (FIG. 3).

It was reported that an ideal answer to this requirement can be found in the Norrish II type photofragramentation of the alkyl or 2 Oxo acetate (alpha keto esters). The Oxo acetates when irradiated with light, the alpha hydrogen abstraction forms a 1,4 biradical that degrades to form a final reaction product. 2 Cyclohexyl Oxo acetates and 2 oxo-2- phenyl acetates have been reported as most suitable precursors for the perfumery applications.

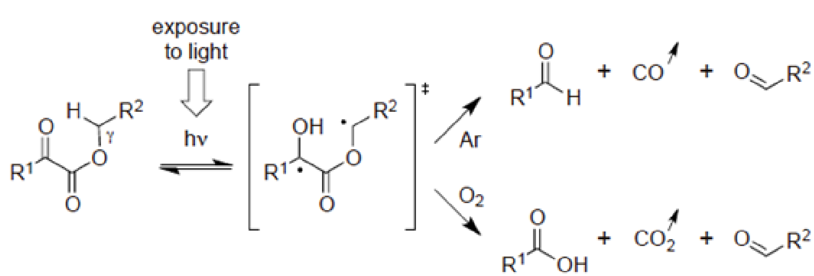

FIG. 3.**Norrish II type photo reaction of 2 Oxo-acetates in the presence of Oxygen.**

One such precursor to be studied with real time conditions using an Oxo complex formed with citronellal. It indicates results of the study of the release and concentration of the citronellal molecule from the precursor exposed to sunlight through a film of an all-purpose cleaner. It was reported that the intensity of the sunlight reaches maximum during noon and the maximum concentration of citronellal released somewhere overlaps with this. Dynamic headspace analysis has shown that this can cause a long lasting effect for the fragrance. Thus it is observed that the Norrish II type photo fragmentation reactions of 2 Oxo acetate complexes are an effective mean of controlling the release of the fragrance compounds.

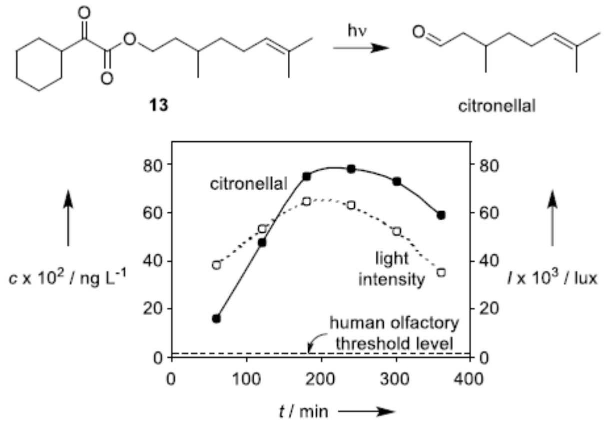

FIG.4**. Study of Citronellal Oxo complex release in sunlight and its concentration.**

Thermo-cleavable Pro-fragrances

Another class of the interesting pro-fragrance molecules is the thermo-cleavable pro fragrances which breakdown as a result of changes in temperatures. The volatile compounds on application and exposure to heat release volatile compounds. It was reported that pyrolysis leads to release of benzaldehyde and pyrazine derivatives at temperatures above 150'C.

Another example was quoted by Chan et. al. The use of sugar derivatives as pro-fragrance molecules has been widely followed. These sugar derivatives are widely available, cheap to procure and environmentally sustainable. Upon heating the sugar derivatives release volatile compounds primarily because of the degradation of the glycoside bonds. Functionally these are alcohols and phenols and aldehydes from cyclical acetals.

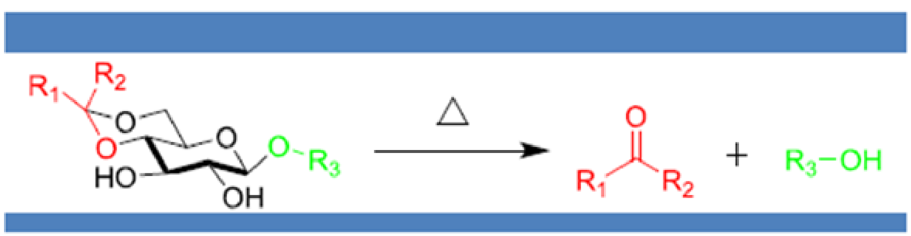

FIG.5. **Breakdown of thermoclevable sugar derivative.**

Enzymatic & Micro organism

An important class of the other triggers that release pro-fragrances are enzymes and microbes. Both of these are part of the ecosystem including nature, plants, water resources, human body etc. These microorganisms are used to cleave selective functions of the pro fragrance molecules with time. One such widely studied family of enzymes is the glucosidases. They are known to break the glycoside bonds and help in releasing mono or di saccharide derivatives. These derivatives can be either mono terpenes, sesqui terpenes or derivatives of phenyl propane . The profragrances based on glycosides can be specially on interest in water soluble applications since they are highly water loving moieties. Ikemoto et.al. reported that these applications are of interest in the Bodycare and cosmetic applications particularly as these products are used primarily on the skin. He synthesized the precursor and studied the action of glycosidase on a sugar profragrances complex. The scheme is represented.

A second class of enzyme called as the Lyases particularly Beta-Lyases is found on the human skin and it is responsible for the generating the thiols and other body odors. It was reported that the pyridoxal phosphate dependent Beta lyases would give pyruvate derivative, a thiol derivative or Alchohol depending upon the precursor. Where it was found that the enzyme was able to produce phenylethylol after prolonged contact with skin. This could find application in deodorants and antiperspirants. The third type of enzyme studied is the lipase which is capable of cleaving the triglyceride molecules. In figure 7 it is shown to trigger cleavage of enol esters.

Polymer based Pro-fragrance systems

Polymers have been widely put to use as a medium for controllable release of fragrances and hence get classified as a pro fragrance precursor. Wie-Hong-Zhu et.al reportedly worked on the synthesis of the polyhedral oligomeric silsesquioxane derivative thiourea compounds which help in linking the volatile carbonyl compounds with spontaneous formation of fragile hydrogen bonds. It was reported that in the study the POSS thiourea complexes were formed consisted of methoxy substituted thiourea, methyl substituted thiourea, unsubstituted thio urea, nitro substituted thiourea and trifluoromethyl substituted thiourea. A comparative study of these and cyclamen aldehyde complexes was made on wall paper substrate with water as humidity agent and triggering of hydrogen bond formation. The below chart summarizes the study and it was observed that the higher concentrations of cyclamen were released from the POSS thiourea fragrance complexes than those without it. The concentrations measured over a period of time were significantly more thus giving a long lasting effect

Materials and Methods

Selection criteria for pro-fragrance technology

The number of fragrance molecules, their complexes are wide employed with different types of precursor molecules. Here we are trying to ascertain what could be the minimum possible criteria for selecting a pro fragrance technology.

Essentially the release of pro fragrance molecules is based upon the breakage of covalent bond between the fragrance and the delivery molecule. Hence the structure of the precursor is of much importance. The precursor must be able to release a broad variety of materials with functional groups such as aldehydes, ketones, alcohols, esters etc. Often it has been found that the precursor will be able to release one type of fragrance molecule. As a fragrance is made up of the many types of molecules with different volatilities. So it makes sense to take the molecules with highest volatility typically from those fitting in top and the middle notes of perfumes and typically delay their release from the substrate.

The below mentioned parameters must be accounted while choosing the pro-fragrance technology.

1) Molecules to be released

2) Environmental conditions

3) Type of Trigger

4) Desired kinetics of Release

Overall the pro-fragrance technologies have chemical links broadly cover two types

1) Dynamic bond formation

2) Non Dynamic bonds

The dynamic ones are those where the bonds are formed in situ between the substrates and the fragrance molecules when a certain reacting substrate is added where as in non-dynamic bonds irreversibly release the volatiles and may need specific synthesis again externally.

Application of the pro-fragrance technology in cosmetics

The application of the profragrances molecules to the cosmetics depends on the type on product that is being designed. It also depends on the type of emulsion which the product actually is. These products could be oil in water, water in oil or multiple emulsions like sunscreen products. Each product has specific requirements and expectations. Therefore, the character of the pro-fragrance carrier also changes. Largely looking at the specific needs of the cosmetic products, it is possible to choose between the precursor molecule and then combine it with the required fragrance molecule. It has been reported by Dr. Lutz et.al that the dynamic chemical linkage works best for the cosmetic applications. The primary aim of his research is to synthesize the surfactant based on imine bondage and how its interactions happen in various commercially used surfactants.

It has been previously reported by Dr. Nicolas Giuseppone et.al. that it is possible to form Dynamic Covalent Amphiphiles (DCA) which are not only biodegradable but also effective work as pro fragrance precursors as well as encapsulation agents.

One aspect of the work relevant to cosmetics that was carried out was to study profragrances made by the covalent reversible bond between the hydrophilic block and the fragrance aldehyde groups. The dyna-blocks created by this interaction are capable of holding the fragrance molecules inside the core. Since they are self-aggregating micellar entities, they will be evenly distributed in the solution and any change in p(H) will lead to the hydrolysis of the Amphiphiles there by releasing the volatile compounds.

The basic mechanism is the interaction of the imine derivatives. Consider a reaction between an aldehyde and an amine molecule. If the reaction is carried out in an organic medium full reaction can be done and nearly all conversion takes place. But it is brought in contact with water again the imine will hydrolyze and give an aldehyde and an amine until a thermodynamic equilibrium is reached.

When the hydrolysis of the M600 Citral is observed in presence of the anionic surfactant, it is observed that it reaches a value of 7. 3Mm.It shows that it undergoes quick hydrolysis initially but stabilizes at certain point thus ensuring that the micelles remain stable even with presence of the anionic surfactants and tend to break only on dilution with excess water. This behavior ensures that the pro fragrance molecules can remain stable in the bodywash formulation and in storage and can effectively give its effect in usage when it is applied in a shower.

Secondly the effect of non-ionic surfactants was also studied with M600Citral.The formulation is tested with composition as follows for both the unbuffered and buffered range. It was reported that the concentration becomes relatively stable after undergoing some initial hydrolysis. Thus the data was instrumental in concluding that the pro-fragrance encapsulation works effectively and stays relatively stable under the influence of anionic and nonionic surfactants that are commercially used in many products. Thus imine linkages capable of forming the Dynamic covalent Amphiphiles offer a lot of flexibility for various kinds of pro fragrance molecules and offer compatibility with different class of surfactants

Conclusions and Discussions

The pro- fragrance technology is an effective mean to deliver long lasting technology on a variety of substrates ranging from wall finishes to cosmetic products as demonstrated by the work done by researchers as previously said. Some important advantages that could arise are better delivery of fragrances, rationalization of fragrance formulation, applicability to baby products or Free from fragrance products where only targeted molecules can be added, delivery of fragrance across multiple product formats in an eco-sustainable way. It could also be used for specific water soluble fragrances as well.

Some of the disadvantages of the pro fragrance technology could be that it cannot be used on conventional fragrance mixtures which have all the functional groups present at the same time. This limitation has led to more commercialization of powdered encapsulation using the sugar based cellulose derivatives which are available in the form of beads which comparatively has higher capacity to load mixed perfumes for various applications.

Nowadays commercially useful profragrances precursors like dodecyl thio damascone is available for use in laundry applications. Also newer and newer technologies capable of carrying more than one fragrance molecule are coming up. There is also ample scope of work to link more than one molecule in the precursor site as some work has been done on cucurbituril molecules which because of its macro structure can hold more fragrance guest molecules and act as fragrance precursor or releasing agent.

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