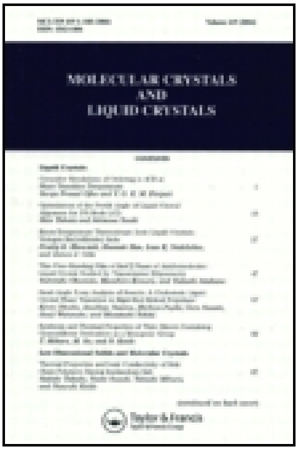

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Gas-Molecular Solid Reactions: Scope and Trends

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GAS-MOLECULAR SOLID REACTIONS : SCOPE AND TRENDS

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Abstract After a brief reminder of presently accepted concepts regarding reactions in organic crystals, the main features of gas-molecular solid reactions are discussed. Presently studied fields are set out and illustrated by numerous examples. The possible industrial applications are considered and some recent attempts are quoted.

INTRODUCTION

Reaction of gases with molecular solids have been reported for more than a century. In 1863 Schmitt[1] studied the addition of bromine vapor to the carbon-carbon double bond of solid trans-cinnamic acid. In 1874 Kolbe[2] succeeded in preparing salicylic acid by heating a mixture of phenol and sodium in the presence of carbon dioxide at atmospheric pressure. In 1884 Pellizari[3] performed the reaction of dry ammonia gas with dried and pulverized phenols and carboxylic acids.

Despite these first results, gas-organic solid reactions have been ignored for a long time by organic chemists. In fact the solid state has been regarded as one which provides nearly complete invulnerability to attack by gaseous reagents. Moreover, this relative unreactivity of solids has been used in some cases as an advantage to protect substances from oxygen or water. For instance, fatty acids were protected from oxidation by incorporating them in the channels of urea crystals in the form of urea inclusion compounds.

It is only from 1960, and the work of Schmidt, that the organic solid state was really taken into account and thoroughly studied. At that time, organic chemists became aware of the great possibilities of the molecular solid state and investigated various types of reaction: solid-state photochemical reactions, solid-state decomposition reactions, solid-solid reactions, solid-fluid reactions.

These last years very few reactions between a solid and a liquid were quoted. On the other hand, gas-organic solid reactions were the subject of numerous experimental studies.

In these reactions the reagents are broken into two distinct phases. The reaction can take place in the fluid phase as well as in the solid phase. In which phase does the reaction take place and when do we know that it is a real solid state process ? These are the first questions that we ask when studying solid molecular chemistry.

CRITERIA FOR GAS-SOLID REACTIONS

Morawetz (1966)[4,5] and Schmidt (1964,1971)[6-8] have suggested some criteria for determining whether a reaction is a true solid-state reaction. A reaction occurs in the solid when :

- the liquid reaction does not occur or is much slower ;
- pronounced differences are found in the reactivity of closely related compounds ;
- different reaction products are formed in the liquide state ;
- the same reagents in different crystalline modifications has different reactivity or leads to different reaction products ;
- the reaction process is related to the crystalline structure of the reactant ;
- the molecules of the product have a preferential orientation relative to the proper crystallographic directions of initial reagent.

It is not always easy to establish such criteria. So a criterion more straightforward in its application was proposed by Paul and Curtin (1973)[9] : "A reaction occurs in the solid if it occurs at a temperature below the eutectic point of a mixture of the starting material and products."

Nevertheless,whatever criteria chosen,it is clear that care must be taken to ensure that a gas-molecular solid reaction takes place in the solid phase.

ANISOTROPY AND ACCESSIBILITY

Contrary to photochemical or thermal reactions which are performed within the molecular solid, gas-molecular solid reactions generally occur at the surface of the solid. Reaction may propagate if the layer of product is continuously removed or, due to its disorganization, allows gas to flow through. In these conditions, are there correlations between crystalline arrangements and reactivity or selectivity ? and what are the main factors to take into account to explain the course of these reactions ?

For example, Paul and Curtin [10,11,12] studying the effect of ammonia on crystalline carboxylic acids observed in the case of 4-chlorobenzoic acid subjected to a low ammonia flow, the (100) face remains clear and transparent while the other faces become opaque. As the reaction proceeds, opacity propagates from the edge of the reacting faces whereas face (100) remains relatively clear. This behavior was interpreted from the crystal structure of 4-chlorobenzoic acid. Carboxyl groups are exposed on all the crystal faces, except on face (100) on which there are the 4-chlorophenyl groups which are turned to the outside. On this face, gas molecules have to cross the layer of substituted aromatic rings before reaching the carboxylic groups which are the reactive sites.

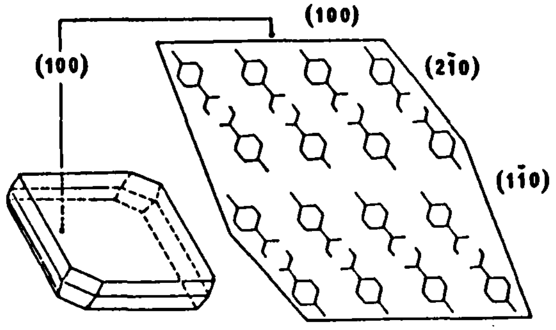

FIGURE 1 Representation of 4-chlorobenzoïc acid crystal

In such chemical transformations, reaction front progression is rapid and occurs almost at the same rate in two directions. The first direction X almost perpendicular to the plane of the aromatic rings, the other,Z,is that of the line joining the two oxygen atoms of the carboxylic group. On the other hand, reaction propagation in direction Y is slow because molecules of ammonia have to cross the layer of aromatic rings. In this direction the reactive sites are protected and the reactivity decreases. Such reactions were called "ditropic" by the authors.

As opposed to these reactions Paul and Curtin[13] consider as "unitropic reactions" those which propagate in only one direction. This is examplified by the reaction of ammonia with single crystals of 1-methyl-2,2-diphenyl-carboxylic-cyclopropane. In these crystals the reactive sites are in the channels oriented in the direction of reaction Y.

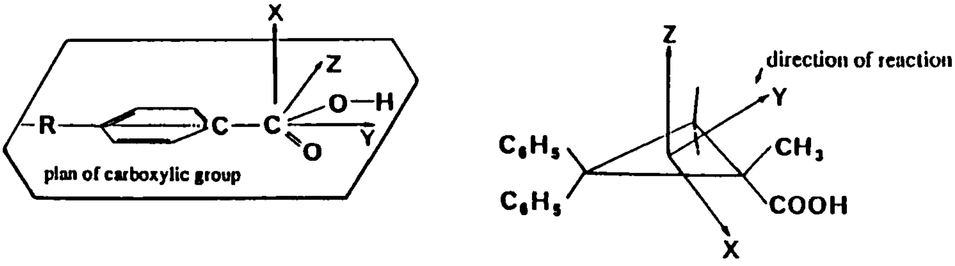

FIGURE 2 Ditropic and unitropic reactions

In the same way Lamartine and Perrin (1977, 1983)^{14,15}, showed the anisotropic behavior of some chlorination reactions of solid phenolic compounds. Firstly, in the case of the chorination of large size single crystals of 2-methylphenol, it was observed that the ratio of orthochlorinated product to parachlorinated product depends on which face of the crystal is exposed to gaseous chlorine. Whatever the conversion ratio, the proportion of the reaction products varies as a function of the crystallographic orientation of reactant surfaces. In this reaction, the diffusion of chlorine is highly improbable since the minimum dimension of a chlorine molecule evaluated by Van der Waals contact radii is about 3.6 Å. and the largest available channel on the structure is about 3.1 Å. In these conditions the variation in selectivity can be explained from the crystal structure by considering the possibilities of access to the ortho or para-position of the 2-methylphenol molecules.

Secondly , high differences in the reactivity of two polymorphic species of parachlorophenol toward gaseous chlorine were reported. Single crystals of the metastable variety react more rapidly than those of the stable form. The stable variety is monoclinic. The hydrogen bonds form chains running along the c axis. The metastable variety is also monoclinic and the structure consists of stacks of tetramers parallel to a axis. For the different faces on the stable variety most of the molecules have their C-Cl and C-OH bonds approximately perpendicular to the face leading to an inaccessible zone for the chlorine. In the case of the metastable variety a great number of molecules have their OH-C...C-Cl axes approximately parallel to the faces. This difference in accessibility and the approach of the chlorine to the reactive centers determine the chlorination reaction rate.

For these gas-molecular solid reactions correlations exists between the crystal structure and the reactivity of solid substances, and between crystal structure and the nature of the products obtained. Thus the topochemical principle stated by Schmidt for photochemical reactions taking place within a solid can be extended to gas-solid reactions which take place at the surface.

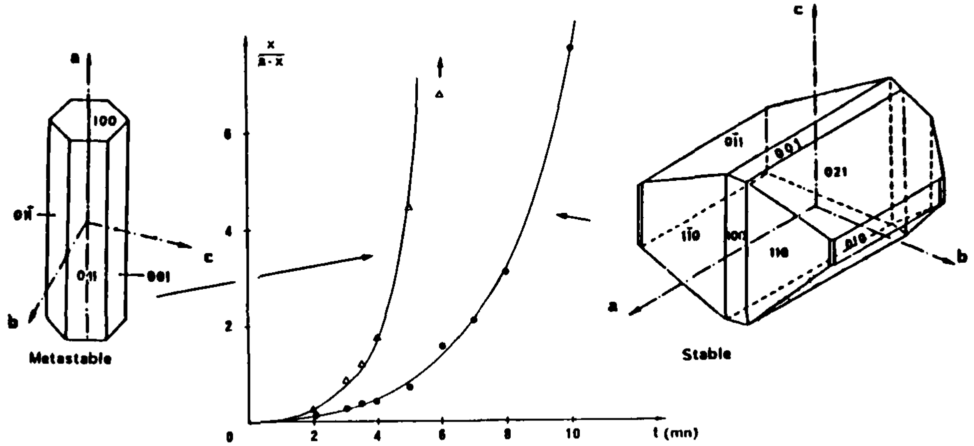

FIGURE 3 Reactivity of stable and metastable crystals of 4-chlorophenol

Even if the diffusion of gas molecules occurs inside the crystal, the accessibility to the reactive centers is the predominant factor to take into account. Very recently, Perrin (1989)^{16} has discussed the so called principle of the "'accessibility to the reactive centers". It seems that this principle may be applied in a general way. It is considered that accessibility should be examined both at the steric level and through the aspect of atomic charges. In other words, it is necessary to take into account both steric and electronic aspects.

MECHANISMS

Relatively few works have been carried out on the mechanisms of molecular solid reactions.Paul and Curtin (1973)^{9} have proposed a four step process for organic reactions induced thermally : loosening of molecules at the reaction site, molecular change, solid solution formation, separation of product.

The first step coresponds to partial unpacking of the crystal at reactive site. The second step is similar to the solution reaction of compounds. In it the chemical reaction occurs. It produces, early in the reaction, molecules of product imbedded in a matrix of starting material. During the third step product accumulates as a solid solution in the parent crystal until the solubility is exceeded and nucleation induces the crystallization of a separate phase. The final step consist of the separation of the product molecules from the reaction matrix and assembly of their own crystalline structure. This step often gives randomly oriented crystals or crystals with an orientation governed by the crystals of the starting material.

For gas-solid reactions the first step also involves diffusion of the gas to the reactive site. Diffusion of a gas into the crystal requires molecular loosening. Thus for gas-solid reaction the molecular loosening step actually involves simultaneous or sequential molecular loosening and diffusion. Byrn (1982)[17] has suggested for desolvation reactions, which are the simplest of the reaction of the type A(s) → B(s) + C(g), a similar mechanism involving four steps: molecular loosening, breaking of the host-solvent hydrogen-bonds, solid solution formation, separation of the product phase.

The molecular loosening step involves nucleation and loosening of the crystal packing so that the solvent can escape. Then the forces that hold the solvent to the host molecules in the crystal are broken. The solvent then leaves the crystal and the product separates. Byrn indicates that the factors influencing the facility of desolvation are the molecular loosening and the strength of the hydrogen bonds of the solvent of the host crystal. The larger the cross-sectional area of the solvent tunnels, the greater the molecular looseness and the easier the desolvation. The strength of hydrogen bonding between the solvent and the host crystal of course affects the ease of removal of the solvent. The weaker the hydrogen bonding, the easier it is to remove the solvent.

In many cases the molecular loosening process cannot be separated from the molecular change. In this way Etter and Vicens (1988)[18] studying the hydrolysis of single crystals of 2-phenyl-3,1-benzooxazin-4-one proposed a mechanism involving at least three steps. First, water vapor penetrates the lattice along channels of free space in the crystal. The motion of water is assisted by formation of hydrogen bonds to nitrogen atoms which are located on the surfaces of the void spaces. The void cavities are not large enough to accomodate the hydrate species so the motion of water is accompanied by crystal lattice degradation and the presence of a phase front. This step is probably the rate determining step. The second step is the product formation which occurs in the disordered reactant lattice at sites containing hydrogen-bonds. The third step would be product segregation which is promoted by the presence of water in the solid state and by water vapor in crystal defect sites, allowing long range motion of the product molecules and the formation of product crystallites outside of the faces of the original reactant crystal.

KINETIC

Solid state reactions show complex rate behavior that is not easily understood and cannot be easily fitted to a single kinetic equation.

The kinetics of the solid state decomposition reactions of drugs have been extensively studied because this data is used to determine the rate constant at the labeled storage conditions. This rate constant is then used to estimate the expiration date of pharmaceuticals. Solid-state decomposition reactions of drugs are often of fractional order . Thus determination of the rate constant at different temperatures is difficult. Cartensen in 1974 [19]has suggested that first-order or zero-order kinetics should be assumed for determination of the activation energy. Thus the rates of decomposition are measured at several temperatures and plotted according to zero order and first-order kinetics. The equation that gives the best fit by statistical tests is then assumed to give the best rate constants.

In the case of gas-solid reactions very few quantitative studies have been carried out and few results are available. The chlorination of 4-chlorophenol powders and single crystals gives interesting kinetic results.[15] Gaseous chlorine reacts with powder of stable and metastable varieties of 4-chlorophenol and gives 2,4-dichlorophenol.The curves giving $x/(a-x)$ as a function of time show that the two crystalline varieties of 4-chlorophenol reduced to fine powder react in the same manner. The logarithmic conversions of these curves are not straight lines. On the other hand, if the quantity $\ln a/(a-x)$ is plotted against time a straight line is obtained which, in a homogeneous medium,is characteristic of a first order reaction. For the chlorination of single crystals the curves $\ln x/(a-x) = f(t)$ giving the conversion ratio against time show that metastable 4-chlorophenol reacts much more rapidly than the stable form. In this case the logarithmic transformation of the curves $x/(a-x)$ against time are straight lines which leads to the following expression of the reaction rate $dx/dt = k\, x/a\, (a-x)$

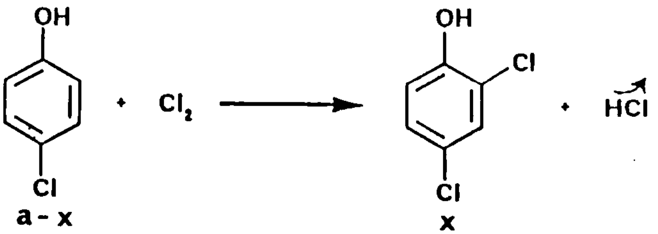

FIGURE 4 Chlorination of 4-chlorophenol

If homogeneous kinetics were concerned it would be possible to state that in the case of powder the rate is proportionnal to the remaining quantity of reagent (first order reaction) and that in the case of single crystals the rate is proportionnal to the remaining amount of reactant and also to the quantity of product formed, which could be hydrochloric acid.

These chlorination reactions are carried out in heterogeneous media. One can ask if homogeneous kinetic equations are valid to describe a gas-solid process and are there specific models which allow us to depict gas molecular solid reactions well.

Very recently Pattou and Perrin (1989)[20-21] have applied the various models proposed in the literature for inorganic solid state reactions and selected the one which seems to be the best adapted to the experimental kinetic results for the chlorination reaction. Both for stable and metastable powders the best model is the Avrami-Erofeev's one with n = 1

$$\left[-\ln\left(\frac{a-x}{a}\right)\right]^{1/n} = kt$$

Powders may be considered as spherical particles between which chlorine molecules can easily penetrate and thus react in a first order way. Pattou and Perrin explain that the chlorine pressure has no influence on the kinetic law by assuming that chlorine molecules easily penetrate the cavities of the powder and are easily adsorbed on the powders. The chlorine quantity near the solid interface can then be considered as constant and the reaction rate does not depend upon it.

For both single crystals, the best model for chlorination is the Prout-Tompkins one

$$\ln\left(\frac{x}{a-x}\right) = k_c(t-t_i)$$

where k_c represents nucleation formation. The reaction occurs through the appearance and development of nuclei. The authors of this study conclude that the reaction is possible because of the existence of some cavities or defects in the solid which allow the reaction to start. Then the molecules of solid produced leave the crystal, carried away by the HCl gas formed during the reaction. The defect grows and further reactions becomes easier and easier.

In the case of catalytic gas-solid reactions,the nature of the catalytic phase, the catalyst/compound interface and the catalyst/product interface play a significant part in the kineticsof the reaction and on the mechanism of the process.[22] In order to explain the experimental data on the kinetics of solid-state catalytic hydrogenation in the system platinum black-thymine and in the system rhodium on carbon-phenols,Filikov and Myasodeov (1988-1989)[23-24] have tested various models. Quantitative models assuming catalyst poisoning have been proposed as well as the diffusion model assuming that the reaction kinetics is determined by the spillover hydrogen concentration gradient in the phase of the organic compound. It was shown that the experimental data obtained could be described only by the kinetic equation of the diffusion model

$$c = b \int_{o}^{1} (1-\exp(-atx))y^{-1}dy$$

The diffusion model has been worked out for a reaction system comprising a crystal of the organic compound with the spherical catalyst metal evenly distributed within the crystals. The calculations for such a system can probably be applied to reactions on the organic compound layer is much greater than the reaction zone radius.

Although some models, proposed in the literature, fit the gas-solid molecular reactions,the area of gas-solid state kinetics remains complex. The kinetic studies can provide information on the mechanisms but as Byrn [17]said "it is not advisable to argue that if a set of data obeys certain kinetics then the mechanism of the organic solid state reaction is established".

TYPES OF GAS-MOLECULAR SOLID REACTIONS

As was just seen in the previous examples, the molecular solid-gas reactions can be carried out with or without a catalyst. The catalyst, either solid, liquid or gaseous, can be used as a distinct phase other than the reagent phase and thus lead to a three phase system.

Most of the gas-solid molecular reactions studied are non-catalysed reactions. Gases like ammonia, amine, chlorine, bromine, iodine, carbon dioxide, water vapor are naturally reactive towards solid carboxylic acids, phenols, olefins, phenoxides, esters, amides, imines.[25-29]. As an example one can quote the very famous bromination of solid chalcones. By exposure of a single crystal of 4,4'-dimethylchalcone to bromine vapour Penzien and Schmidt (1969)[30] have obtained the dibromo-derivatives. The addition of bromine proceeds by trans-addition to the carbon-carbon double bond. The dibromo-derivative obtained is optically active . The optical yield is about 6 %. The chalcone molecule is non planar in the asymmetric crystal and the finite enantiomeric excess can be interpreted as resulting from the difference in the bromine attack on the two faces of the molecule. The asymetric bromination of dimethylchalcone was the first successful asymmetric synthesis carried out by reaction of an achiral gas with a chiral structure crystal. By incorporating a small quantity of optically active dibromo-derivative in the 4,4-dimethylchalcone Green, Lahav and Rabinovich (1979)[31] have improved and increased the optical yield by 25 %. In a recent discussion of these works, Addadi, Cohen, Lahav and Leiserowitz (1986)[28] mentioned that the enantiomeric excess obtained proved very sensitive to the experimental conditions. High excess was obtained only when the reaction rate was kept low, by diluting the bromine with an inert carrier gas. It seems that this is because of melting at high rates. This shows that gas-solid reaction can proceed with high specificity, but careful control of reaction conditions may be required.

Gas-solid additions and gas-solid substitutions can afford very interesting possibilities in organic syntheses. This was recently shown by the works of Kaupp and Matthies (1988)[32]. Powdered N-vinylphtalimide reacts almost quantitatively with gases like HBr, HCl, HI and Br_2 and gives the crystalline 1-bromo-, 1-chloro-, 1-iodo- or 1,2-dibromoethylphtahlimide. In solid state conditions only crystalline addition products are formed,while in solution oligomers and polymers are produced. Similarly, crystalline N-vinylsaccharin reacts with the same gases to give the corresponding products very fast. Highly reactive and highly sensitive products are obtained very easily on a preparative scale. They may be used as precursors for substitution reactions in organic syntheses[33,34].

A major benefit of these gas-molecular solid reactions is shown by transformation of N-vinylpyrrolidinone. This compound polymerizes very rapidly in liquid state or in solution when traces of acid are present. The use of solid-gas techniques is unavoidable if the monomeric adducts with polar gases are to be synthesized.

Kaupp and co workers have generalised these gas-solid reactions further to crystalline enamides, enamines and S-vinyltioethers and demonstrated their high synthetic potential. Polar gases HBr, HCl, HI and $HSCH_3$ react at 1 bar and temperature from 40 to -80°C with crystalline materials,usually in the Markovnikov orientation. However, the S-vinylthioether to $HSCH_3$ addition constitutes the first example of a solid-gas addition with anti-Markovnikov orientation.

Supramolecular systems as well afford feasibility of new gas-solid reactions. Bavoux and co workers (1988)[35] have synthetized supramolecular systems and studied their reactions with gaseous chlorine. Two supramolecular systems were prepared; 3,5-dichlorophenol-18-crown-6-ether-water, 1:1:1, and 3-methyl-2-isopropylphenol 18-crown-6-ether-water 2:1:2. Very different reactivities towards chlorine were observed depending if the phenol molecules are pure or complexed. The changes in phenol molecule reactivity and selectivity are due to surroundings modification of these molecules in the pure product crystal and in the supramolecular crystal. So, by gas-solid reaction, one can envisage topologic control of the reactivity of molecules included in supramolecular systems and control of the selectivity of their reactions.

As an example of catalysed gas-solid reactions one can quote hydrogenation of aromatic compounds. In the case of hydrogen it is necessary to use a catalyst in order to obtain reactive species because hydrogen is not naturally reactive as chlorine or bromine are. The first solid state hydrogenation of an organic compound was achieved with thymol in order to prepare menthol.[36] To perform this reaction, thymol is ground to a fine powder and mixed with the catalyst. The conversion ratio at 20°C under 1 bar hydrogen pressure is 99 % with platinium/carbon as a catalyst. Similar results obtained with a great number of solid phenols prove that it is possible to hydrogenate solid aromatic compounds under mild conditions : room temperature and one bar hydrogen pressure. This confirms enormous reactivity of the solid state towards gases because in homogeneous media hydrogenation occures only at high temperature and at high pressure.

In three phase systems, organic solid/solid catalyst/gas, the contacts between the catalyst and the organic reagent are poor. To explaine their results Lamartine and co-workers (1979)[37] have assumed the presence of "activated hydrogen" at some distance from the catalyst. The molecular hydrogen on contact with metal gives "activated hydrogen". This hydrogen is transferred on the surface or in the bulk. This is the first spillover effect. By means of contact between support and organic solid, activated hydrogen moves across the organic reagent and reacts. This is the second spillover effect. So the support and the organic reagent make up solid phases which allow the migration of hydrogen in its "activated" state. Experiments carried out with deuterium as gas (Sabbra, 1989)[38] confirmed this double spillover effect.

Recently, Kaup and Matthies (1988)[32] have performed the hydrogenation of cinnamic acid doped with palladium. The traces of palladium are uniformly distributed in the crystals. In this case one may consider firstly the migration of non-activated hydrogen within the organic solid,which acts both as a reactant and catalyst support, and secondly the migration of the metal or of the activated hydrogen within the crystal to allow the reaction to proceed.

The significance of catalysed gas-solid reactions was also shown in the field of alkylation reactions[39]. In the presence of solid catalysts, like silica-phosphoric acid catalyst, alkylation of solid phenols with alkene gases was carried out in mild conditions. The reactivity and selectivity of the solid phase are a function of the nature and of the quantity of catalyst. For the reaction phenol-isobutene gas, the ratio O-alkylation/C-alkylation is 7 and the main product formed is tert-butylphenylether.

Photo-induced processes take place in the gas-solid reactions, and play an important part in the oxidation processes of molecular solids. For example, oxidation in light and air is a prime cause of drug instability because it is impossile to remove it totally. Several authors have studied the behavior of solid drugs, vitamins and dyes on irradiation in the presence of oxygen. It would appear that oxidation is catalyzed by traces of metallic impurity, is accelerated in a high humidity atmosphere . Different crystal forms exhibit different oxygen reactivity[17].

In general when organic solids are irradiated free radicals are formed. These free radicals usually have the same structure as the parent molecule except that a single hydrogen atom has been removed by irradiation. A free radical contains an unpaired electron. It disappears by reacting with another free radical. Since the free radicals, like the parent molecule, are usually held fixed in the crystal they are very stable in most crystalline substances and are able to react with gases. This was exemplified by the reaction of irradiated aliphatic monoamides and fatty acids with ambient gases such as oxygen, nitric oxide, nitrogen dioxide and sulfur dioxide. Adler[40] has shown that gases diffuse into substances that have a "stacked bilayer" type of crystalline structure and react with any free radicals that may be present.

The advantage that solid-state oxidation can have over the corresponding solution reaction is well illustrated by the works of Desvergne and co-workers (1974)[41]. Irradiation of crystals of trans-stilbene and dietylstilbesterol in the presence of oxygen give good yields of the corresponding ketone or aldehyde,while oxidation under similar conditions in solution yields many products.

INDUSTRIAL APPLICATIONS

At the end, I would answer the questions, can gas-molecular solid reactions be carried out on an industrial scale and what are the possible industrial applications?

The Kolbe-Schmitt[42] reaction is a good example of gas-solid reaction carried out on an industrial scale. In this reaction, the solid alkaline phenoxides, submitted to the action of carbon dioxide, yield ortho and parahydroxybenzoïc acids. The orthohydroxybenzoïc acid,or salicylic acid,is by far the most important as it yields aspirin by acetylation of the phenolic function.

Modern methods of commercial manufacture of salicylic acid still employ the basic Kolbe-Schmitt reaction. The solid phenoxide is prepared by mixing phenol and soda in water, drying under atmospheric pressure and then under vacuum. The dry sodium phenoxide is placed in a reactor called a "carbonator" with dry carbon dioxide at 10 bars. Air is excluded to minimize oxidation and the formation of coloured compounds. After acidification and acetylation aspirin is obtained.

Industrial production of parahydroxybenzoïc acid is done in the same way. The reaction is oriented para to OH group by replacing solid sodium phenoxide by solid potassium phenoxide.

Solid-gas processes have also been taken into account for the production of alkyl phenols and alkyl aryl ethers [43]. It is well known that, depending on the experimental conditions,O-alkylation or C-alkylation of phenols occur . A low reaction temperature and a small proportion of catalyst lead mainly to O-alkylated products. The organic solid state provides best conditions to produce the ether. For example tert-butylphenylether is produced in a semi-batch reactor. Doped phenol powder is placed and stirred at 8°C in the reactor. Addition of the isobuten at l bar pressure yields a fluid phase mainly consisting of tert-butylphenylether.

The use of solid catalysts in the alkylation reactions has the advantage of not giving polysubstitution and polymer derivatives. To achieve solid state alkylation with solid catalyst on a semi pilot plant scale, two reactors are currently considered: a batch reactor and a plug flow reactor. In a batch reactor, no matter enters or leaves the reactor mixture during the reaction. In a plug flow reactor the composition of the matter varies from point to point along a flow path. The performance of the reactor is dependent of the rate of reaction , the extent of reaction, the reactor volume and the feed rate. All this data is currently under investigation in our laboratory to design a chemical reactor for solid state alkylation of phenols.

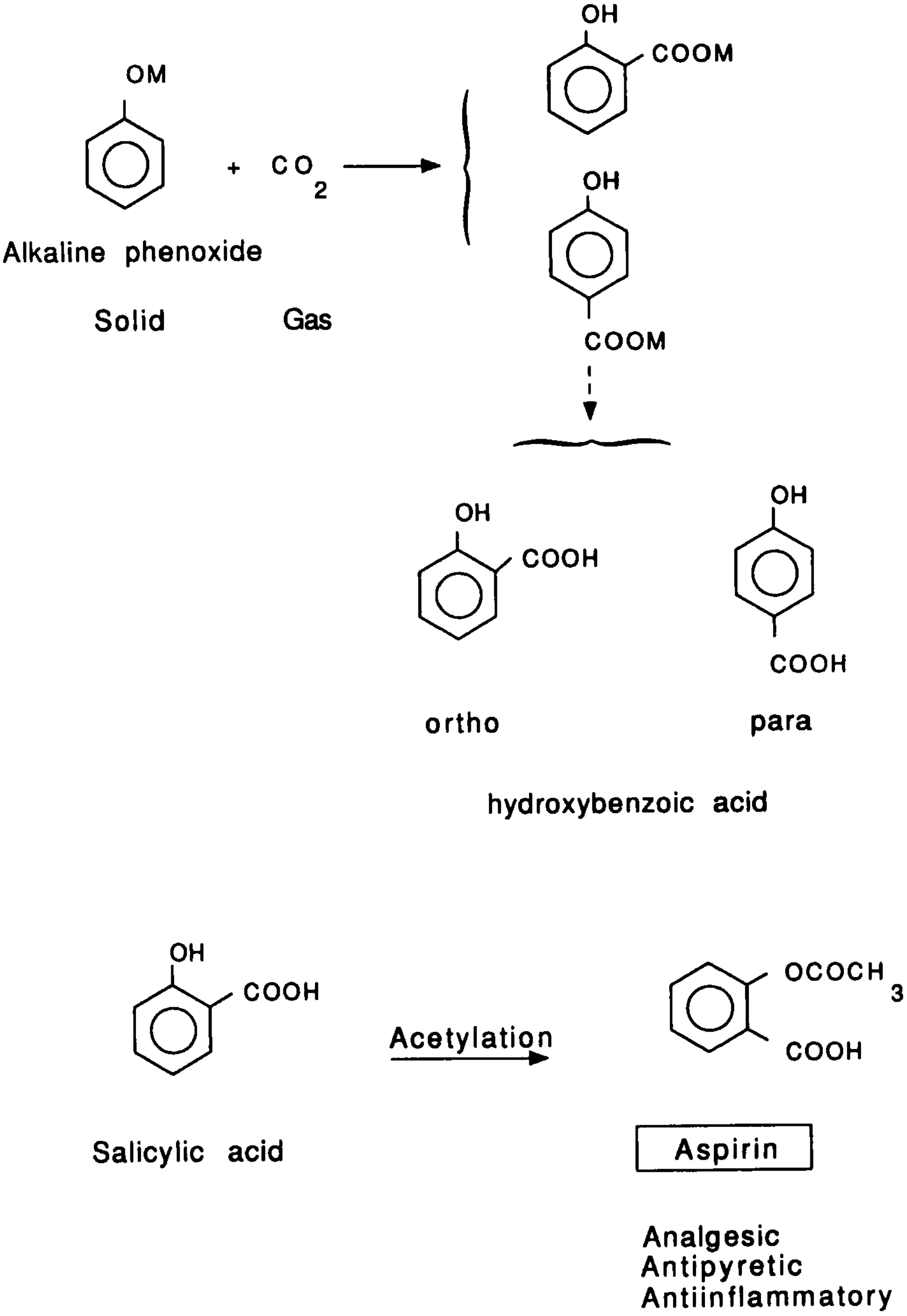

FIGURE 5 Kolbe-Schmitt reaction

The solid state affords particular advantages (no solvent, regioselectivity, suppression of polymerization...) which provide industrial development opportunities. The industrial development of gas-molecular solid reactions could be carried out as well for the production of new higher value materials as in the improvement of processes.

CONCLUSION

The reactivity of gases towards moleculr solids has been established in numerous reactions. With or without catalyst, gases react with molecular solids. In some cases an initiator like light is necessary to obtain a reactive system.

Most gas-solid reactions are easy to bring about. Reactivity and selectivity are dependent on the accessibility of the reactive centers. The anisotropy of these reactions has been used to an advantage in asymmetric synthesis, organic synthesis and in reactions of supramolecular systems. Reactions with water vapor and oxygen are determining factors for the shelf life of drugs and play an important part in the stability of vitamins and dyes. So investigation fields are numerous and today we can say with Paul and Curtin "Gas-solid reactions offer unique possibilities in organic chemistry."

Gas molecular solid reactions are not purely academic reactions. Although few industrial applications exist, it is possible to consider gas-molecular solid reactions in various processes. This opens a large investigation field to those who are concerned with industrial development.

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