Phototransformation of some pesticides[†]

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The photochemical transformation of two fungicides, viz. fenarimol (1) and chlorothalonil (6), two herbicides, viz., met-sulfuron methyl (15) and fluchloralin (20), and one insecticide, imidacloprid (26) has been carried out, the results of which form the subject-matter of the present review article. The degradation products are characterized on the basis of spectro-scopic evidence. The use of sensitizers like TiO_2, KNO_3, H_2O_2 is observed to enhance the photolytic rate. The results indicate that some of the photometabolites could also be formed through biotic processes. It also reveals that photochemical trans-formation leads to detoxification of the pesticidal molecules. The phototransformation processes involve N-dealkylation, nitro group reduction, cyclization, dimerization, oxidative cleavage, homolytic cleavage, dechlorination, decarboxylation and dehydration types of reactions.

The use of pest control chemicals to protect the crops from damage is unavoidable as we need the maximum yield possible to meet our sharply increasing demand for food grains. Pesticides are also used in public health programmes, household pest control and also for controlling veterinary parasites. Besides controlling pests like insects, diseases, etc., the pesticidal chemicals have the potentiality of affecting the life and environment adversely. As we know, all pesticidal molecules after application are exposed to various biotic and abiotic components of the environment and are thus subjected to various physical, chemical and biological transformation processes. It has been demonstrated over the past few years that photochemical reactions play a key role in environmental degradation or detoxification of various anthropogenic chemicals including pesticides that contain organic chromophores or metal-organic complexes capable of absorbing light energy directly. Indirect photolysis or photosensitization is important especially for the pesticidal molecules having no chromophoric groups. Sensitization process may be catalytic in nature when the chromophore in the sensitizer molecule is regenerated by the process of energy transfer and cyclic redox reactions[1]. Photosensitizers transfer the absorbed light energy to the acceptor molecule of pesticides. Substantial enhancement in the photodegradation of pesticides has been observed by soil organic matter like fulvic acid and humic acid; dyes like rose Bengal, methylene blue; pigments like chlorophyll, xanthone; ketones like acetone, acetophenone, benzophenone; secon-dary plant metabolites like riboflavin, tyrosine, etc.[2,3]. Moreover, the surfactant molecules (e.g., Triton-X-100) used in various pesticide formulations may also act as photosensitizer[4]. The first chemical step in a photoreaction involves bond cleavage, usually homolytic, which yields free radical species. The energy equivalent in radiation of wavelength at 300 nm (95 kcal mol^{-1}) is sufficient to disrupt most covalent bonds. Various organic and inorganic free radicals (e.g. CH_3, R, RO, ROO, NO, NO_2, OH, etc.) are often produced in environmental photoreactions along with other reaction products, particularly oxidants. The oxidants participate in important non-radical reactions and also frequently generate new radicals, thus serving as radical reservoirs. The potential radical reservoirs in natural waters include peroxide and hydroperoxide reactions and reduced metals like iron(II), CuCl, etc.[1].

Environmental photochemistry of pesticides is complicated as because these molecules may interact with many environmental components. Moreover, photolytic reactions are greatly influenced by meteorological conditions, especially sunshine hours and the results may vary with time of experiment. Therefore, most of the studies have been restricted to laboratory conditions or model experiments which may provide valuable information regarding the environmental behaviour of these molecules. A limited study is available on the photodegradation of pesticides under environmentally relevant gaseous state[5]. Studies in solution phase, however, may be undertaken in open or partially open glasswares placed under direct sunlight. Quartz or borosilicate glasses which are transparent down to 230 and 290 nm respectively, may be used for this purpose. Aqueous solution of pesticides or solution in organic solvents (e.g. hexane, methanol, isopropanol, etc.) having low absorbance in UV region is generally used for such study. For reproducible results, pesticide solutions are generally irradiated under laboratory condition using a photoreactor

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[†]Dedicated to our teacher, Professor D. Nasipuri with profound regards on the occasion of his 75th. birth anniversary.

consisting of a reaction flask fitted with mercury vapour lamps or germicidal lamps that are rich in radiation in the range 240–260 nm[6]. Xenon lamps may also be used, as its spectral energy distribution is almost similar to that of sunlight[7] but with higher intensity. Soil photodegradation studies on pesticides have been carried out on thin layers of soil coated on glass plates. However, the usefulness of such type of experiment is often debatable[5]. Transformation of pesticides also occurs in plants but it is difficult to differentiate between photochemical and other transformation processes occurring in plants.

Various types of reactions have been observed in the phototransformation of pesticidal molecules. However, photooxidation is one of the most prominent means of photodegradation initiated by various reactive species like singlet oxygen, free radicals, organic hydroperoxides, hydrogen peroxides, etc.[2,8]. Photochemically induced isomerization, dimerisation, dechlorination are common reactions usually suffered by organochlorine insecticides[9–11]. Organophosphorus pesticides undergo photodegradation mainly by ester cleavage, reduction, oxidation of thioether group, isomerization, dehalogenation, dehydrohalogenation, dealkylation, cyclization, dimerization, etc.[12]. Carbamate pesticides undergo hydrolysis, oxidation, methylation, rearrangement reactions[13] when exposed to light. Pyrethroid insecticides degrade mainly by hydrolysis of the ester bond, cis-trans isomerization, carboxylation, reductive dehalogenation[14] in the process of phototransformation.

The toxic action of pesticides is desirable for a certain period to control or kill the target organism and after this period it is also desirable that the molecule be deactivated through various transformation processes to some non-toxic products. Several popular organochlorine pesticides like aldrin, dieldrin, DDT, endrin, heptachlor, etc. have been phased out due to the undesirable persistence of their toxic residues in the environment. Therefore, for proper recommendation as well as for environmental safety evaluation of a pesticidal molecule in a particular agroclimatic condition, researches are generally conducted to understand their nature of persistence as well as the nature of transformation products formed in various components of the environment, viz. soil, water, plant, etc. Moreover, the transformed products formed are not always non-toxic, they may be equally toxic or even more toxic than the parent pesticidal molecules. Among the several transformation processes as mentioned above, photochemical and microbial degradation processes play major roles for environmental detoxification of pesticides. The results of photochemical and microbial transformations of some selected pesticides carried out in our laboratory have already been reviewed earlier[15]. We, in

India, receive a huge quantity of solar energy which is a rich source for enhanced photochemical reactions of pesticides as compared to that occurring in other temperate countries. Therefore, it is expected that the efficiency of photochemical processes of degradation may sometimes be greater than that occurring in microbial processes in our agroclimatic conditions. With these objectives in view, our laboratory has been pursuing researches on some selected pesticides with special emphasis on the photochemical transformation of pesticides in solution phase exposed to UV-light under laboratory condition and also exposed to direct sunlight under natural condition. A brief account of such studies forms the subjectmatter of the present article.

Fenarimol

Fenarimol [(±)-2,4'-dichloro-α-(pyrimidine-5-yl)benzhydryl alcohol, 1], a broad spectrum fungicide, has been shown to be effective against powdery mildew, rust, scab and dollar spot diseases of both fruit and ornamental plants and is known to undergo rapid degradation on exposure to sunlight[16].

The photodegradation of aqueous alcoholic solutions of fenarimol (1) under the influence of UV and sunlight was studied in our laboratory[17]. UV-irradiation of aqueous methanolic solution of 1 for 24 h yielded two photoproducts, identified as 2,4'-dichlorobenzil (2) and p-chlorobenzoic acid (3) while that of aqueous isopropanol solution of 1 yielded two additional products, viz. 2,4'-dichlorobenzophenone (4) and o-chlorobenzoic acid (5) alongwith 3. Sunlight irradiation of aqueous methanolic and isopropanol solution of 1 afforded five photoproducts, out of which three products were identified as 3, 4, 5 and the other two compounds could not be characterized due to paucity of materials. A plausible mechanism of the formation of these photoproducts from 1 is presented in Chart 1.

Chlorothalonil

Among the chlorinated aromatics, nitriles represent an increasingly important group of pesticides of which chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, 6) is a broad spectrum fungicide used against many plant pathogens affecting a large number of agricultural crops. Earlier studies[18–21] on the photochemical transformation of 6 in different organic solvents, viz. benzene, dichloromethane, ethanol and methanol have been reported. In benzene, 6 was photodecomposed by sunlight or UV-light[17] to form the products 7 and 8, while in dichloromethane 6 was transformed[19] to 9 and 10. In our laboratory[22], the phototransformation of 6 was carried out in ethanol and methanol under UV-irradiation ($\lambda \geq 250$ nm) yielding three
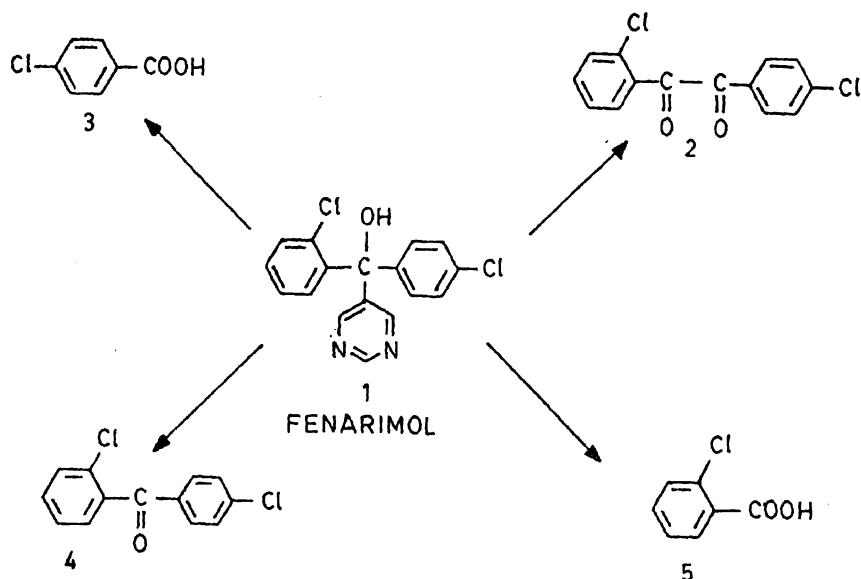
Chart 1. Transformation of fenarimol under UV and sunlight.

photoproducts (**11-13**) as shown in Chart 2. The products formed from **6** appeared to be the results of several reactions in complex sequences. The primary photochemical reaction is the homolytic cleavage of 4-Cl–C bond followed by alkylation of the α-radicals (R-ĊHOH, where R may be H or CH₃) derived by photoirradiation of alcohols with concomitant formation of HCl in the solution. Although the nitrile group cannot be easily substituted and does not un-

dergo changes but in this case the stereochemically ideal proximity of the nucleophile resulted in an accelerated irreversible condensation with the neighbouring alcohol group to yield the hydrolytically sensitive imidines producing 4,5,7-trichloro-6-cyano-3-methyl-1(3*H*)-isobenzofuranone (**11**) in case of ethanol and 4,5,7-trichloro-6-cyano-3,3-dihydro-1-isobenzofuranone (**14**) in case of methanol. When more than one Cl is substituted both equivalent Cl of **6** are assumed to
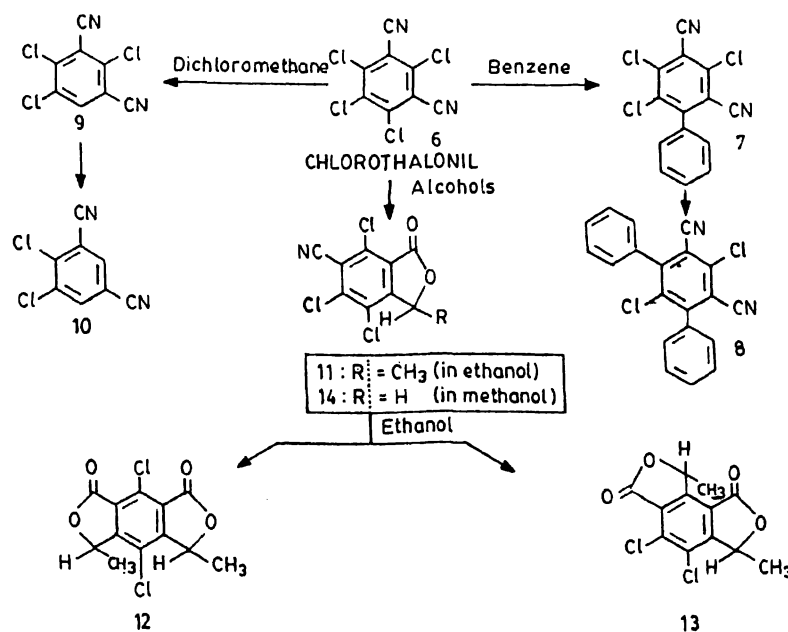

Chart 2. Photochemical transformation of chlorothalonil in different solvents.

be replaced. So cleavage of the 4- and 6-Cl–C bond following the same mechanism resulted in the formation of 4,8-dichloro-3,5-dimethyl-3H,5H-benzodifuran-1,7-dione (12). The isomeric product (13) was also reported[20] earlier. It was also observed that due to the replacement of chlorine atoms, the products (11, 12, 14) exhibited lower fungitoxic action[22]. It can thus be understood that there is enough scope to utilize the UV-rays for detoxification of the fungicide residues.

Metsulfuron methyl

Metsulfuron methyl (methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazine-2-yl)amino]carbonyl]amino]sulfonyl]benzoate, 15) is one of the twenty commercialized members of sulfonyl urea herbicide group, newly introduced in India by E.I. Du Pont de Nemours and Co., which is reported to be effective against selective broadleaf weeds in wheat, barley and some other crops[23]. Several studies[24–26] revealed the hydrolytic dissipation of these herbicides but little is known about the effect of light on their degradation. A preliminary study was conducted in our laboratory[27] to understand the effect of UV-light on the degradation of 15 in aqueous solution. The study indicated a degradation of about 50% of the herbicide under UV ($\lambda \geq 290$ nm) irradiation for 15 h in aqueous solution. The irradiated solution of 15 upon extraction, concentration followed by chromatographic frac-
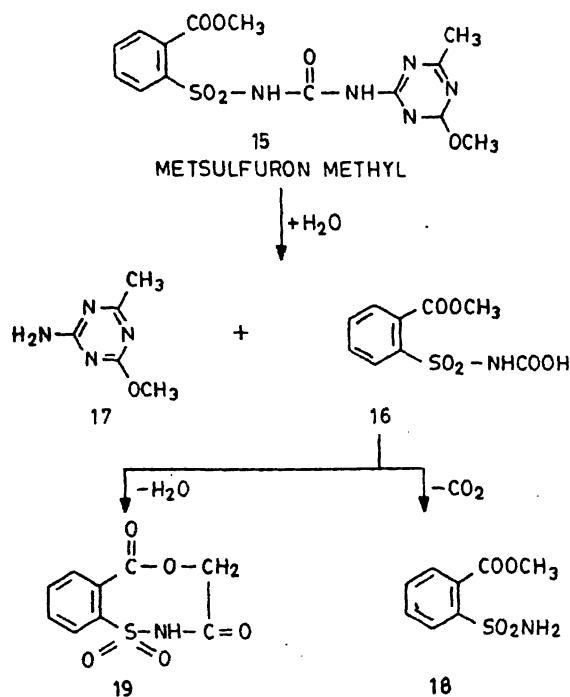
tionations yielded three photoproducts of which two could be identified (18 and 19) on the basis of their physical and spectral properties. The photolysis of metsulfuron methyl (15) initiated by the hydrolytic cleavage of the sulfonylurea bridge to form the corresponding phenyl sulfonyl carbamic acid (16) and s-triazine amine (17) derivatives. The carbamic acid (16) suffered further decarboxylation and dehydration respectively under UV-irradiation to form the corresponding phenyl sulfonamide derivative (18) and a cyclized derivative (19), possibly formed by dehydration of 16 (Chart 3), the latter being obtained as a major phototransformation product of 15.

Fluchloralin

Fluchloralin [N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-(trifluromethyl)aniline, 20], a member of substituted dinitroaniline class, has been extensively used to control various weeds[28]. Niles and Zabik[29] first sudied the photodegradation of 20 under different experimental conditions and found it to be susceptible to sunlight. However, a detailed study on the photodegradation of 20 still remains obscure. In view of the above fact, the photodegradation study of 20 was undertaken[30] under UV and sunlight in aqueous methanol (80%) in the presence and absence of TiO_2.

The photolyzed (both UV and sunlight) aqueous methanolic solution of 20 in absence of TiO_2 yielded four photoproducts (21-24), while in presence of TiO_2, 20 led to the isolation of a new photometabolite (25) in addition to 21-24 (Chart 4). The major degradative pathway involved N-dealkylation, nitroreduction, cyclization and dimerization. Interestingly, 22 and 24 were reported as microbial metabolites in our previous study[31]. However, the photoproduct 25 was reported for the first time for fluchloralin (20).

Imidacloprid

Imidacloprid [1-(6-chloronicotinyl)-2-nitroiminoimidazolidine, 26] belonging to the class of chloronicotinoid[32], is a new insecticide with high activity against various sucking pests[33], including rice hoppers, aphids, thrips and white flies. It also finds use against soil insects, termites and some species of biting insects, such as rice water weevil and colorado beetle[34].

The photolysis of imidacloprid (26) in aqueous solution was studied. Irradiation at 290 nm resulted in 90% substrate transformation in 4 h[35]. The main photoproducts were identified as 6-chloronicotinaldehyde (27), N-methylnicotinamide (35), 1-(6-chloronicotinyl)imidazolidone (33) and 6-chloro-3-pyridylmethylethylendiamine (34). Besides, some

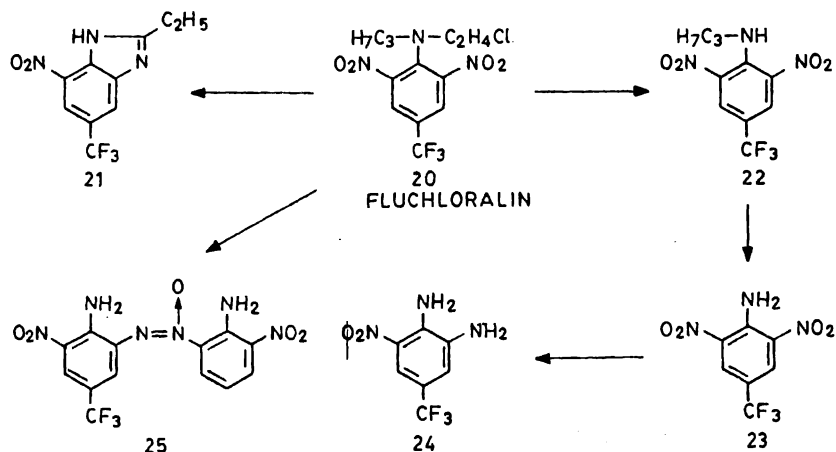Chart 3. Photolysis of metsulfuron methyl in aqueous solution.

Chart 4. Photometabolites of fluchloralin

minor products (30-32) were also reported to form under UV-irradiation (Chart 5). In our laboratory[36], imidacloprid solution in acetonitrile-water (1 : 9) was exposed to UV-light as well as under direct sunlight. The use of sensitizer molecules like TiO_2, H_2O_2, KNO_3 at different concentrations proved to be effective in substantial enhancement of the rate of photolysis of 26. The overall rate of photolysis was higher under UV-irradiation than that observed under sunlight. Three photoproducts were isolated from the solution irradiated by UV-light and also by sunlight but the rate of formation of photoproducts was higher under UV-light. The products were identified as 33, 1-6[(6-chloro-3-pyridyl) methyl-*N*-nitro-2-imidazolidin(4,5)ene-imine (29) and 6-chloronicotinic acid (28) (Chart 5). Product 33 was formed

by >N–NO$_2$ bond cleavage, abstraction of hydrogen atom from the molecule forming the imine which underwent hydrolysis in presence of UV-irradiation[35]. Product 29 was formed by hydroxylation of imidazolidine ring by hydroxyl radical and consequent elimination of a water molecule[37]. Compound 28 was reported to be formed by the oxidative cleavage of the methylene bridge to form 6-chloropicolyl alcohol[35] and further oxidation to form 6-chloronicotinic acid (28) via 6-chloronicotinaldehyde (27). A plausible pathway of phototransformation of the insecticide is presented in Chart 5.

It has been revealed from the above studies that some of the phototransformed products are found to be identical with
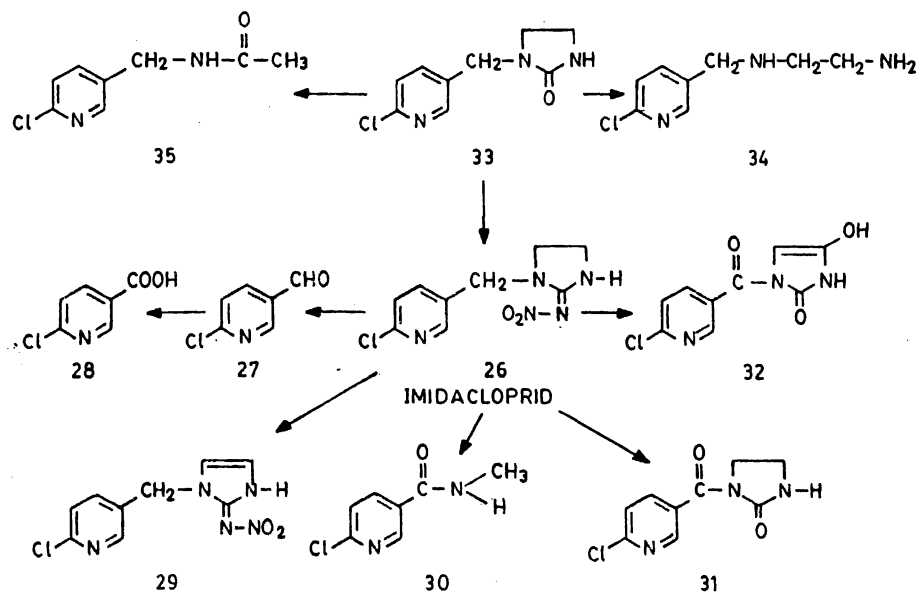

Chart 5. Photodegradation of imidacloprid.

the products obtainable from microbial degradation. Thus fluchloralin (20), on photochemical transformation yielded two photoproducts which were found to be identical with those obtained from microbial degradation in our laboratory[31]. Therefore, it is quite reasonable to expect that these compounds may be found in different environmental components, viz. soil, plants, water, etc. However, it has been observed that many of the phototransformed products are entirely different from those obtained from microbial degradation processes. It has also been noticed that the phototransformed products so formed may not be non-toxic in nature and therefore these require toxicological evaluation from the viewpoint of environmental safety. We found from our own study that three phototransformed products of chlorothalonil (6) were less toxic than the parent compound[22]. A similar type of detoxification of a dinitroaniline herbicide by microbial degradation was also observed in our earlier studies[38]. Thus, the fate and behaviour of pesticides in the environment cannot be assessed only by monitoring the parent pesticidal molecule. It should include their metabolites and other degradation products as well. Also, for judging the environmental toxicity of pesticides, the picture is incomplete without having a detailed toxicological investigation on the degradation products. Therefore, such type of experiments on pesticide transformation in laboratory or under simulated conditions are of paramount importance for evaluating environmental safety of pesticides.

Acknowledgement

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