Russian Chemical Reviews **77** (10) 909 – 926 (2008) © 2008 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2008v077n10ABEH003805

Photocatalytic transformations of organic sulfur compounds and H_2S

A V Vorontsov

Contents

I.	Introduction	909
II.	Classes of sulfur compounds studied in photocatalytic processes	910
III.	Products of photocatalytic reactions	913
IV.	Kinetics of photocatalytic oxidation	918
V.	Deactivation and reactivation of catalysts	922
VI.	Conclusion	924

Abstract. Modern views on the products, pathways and kinetic features of liquid- and gas-phase photocatalytic reactions of sulfur compounds in the presence of heterogeneous and homogeneous photocatalysts are generalised. Attention is focused on the aliphatic and aromatic reduced sulfur compounds and pesticides. The reaction rate in the liquid and gas phases is analysed as a function of solution pH, temperature, catalyst content, substrate concentration, solvent type, air moisture and added oxidants. Photocatalyst deactivation and the ways for recovery of its activity are considered. The bibliography includes 130 references.

I. Introduction

Photocatalysis is a frontier field of chemistry that considers photochemical reactions initiated by irradiated photocatalysts. Photocatalysis can also be considered as the catalysis of reactions that involve light quanta as a reactant. The key difference of photocatalytic reactions from classical photochemical reactions lies in the fact that light is absorbed by a catalyst rather than by reactants, which is followed by the initiation of reactant transformations by the catalyst. According to the definition given by V N Parmon, photocatalysis means 'a change in the chemical reaction rate under the action of light in the presence of substances (photocatalysts) that absorb light quanta and take part in chemical reactions of reactants, being repeatedly involved in intermediate interactions with the latter and recovering their chemical composition after each cycle of these interactions'.[1] Thus, photocatalytic processes involve the following stages: (i) light absorption by catalysts; (ii) intermediate chemical reactions involving excited a photocatalyst and reactants; (iii) photocatalyst regeneration after the transformations. Photocatalytic reactions represent a special case of photosensitised reactions, *i.e.*, photochemical or photophysical changes in a substance that occur as a result of the light absorption by another substance called the photosensitiser.[2] Photosensitised chemical reactions in which a photosensitiser is not consumed when involved in intermediate chemical reactions with reactants are photocatalytic reactions. To answer the question which photosensitised reactions should be classified as photocatalytic reactions, their mechanisms should be considered.

After the absorption of a light quantum, a photosensitiser passes to an electronically excited state. An excited photosensitiser can initiate chemical transformations of reactants *via* either the electron transfer or the transition of excitation energy. The electron transfer is undoubtedly a chemical process. The excitation energy transfer can be considered as a photophysical process because it leads to another (excited) electronic state of the same reactants.[3] Thus, photosensitised reactions with electron transfer should be considered among photocatalytic reactions and those with energy transfer should not.

However, investigation of a conventional photosensitised reaction, the transformations involving mercury atoms in the excited state [$Hg(^3P_1)$], has shown that they can involve the formation of exciplexes with the binding energy up to 86 kJ mol^{-1} (Ref. 4). In the mercury-sensitised arene photolysis, triplet exciplexes of mercury and arenes with the binding energy of 125 kJ mol^{-1} were found that were responsible for the cleavage of C–C, C–N and C–O bonds.[5] The intermediate formation of stable exciplexes with the binding energy that fits the range of chemical bonds should be considered as an intermediate chemical reaction. Hence, photosensitised reactions with energy transfer can also be classified as photocatalytic reactions provided the excited photosensitiser forms relatively stable complexes with the reaction participants. Photosensitisers discussed in the present review pertain to photocatalysts because in the described reactions they are involved in

A V Vorontsov G K Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, prosp. Akad. Lavrentieva 5, 630090 Novosibirsk, Russian Federation. Fax (7-383) 333 16 17, tel. (7-383) 326 94 47, e-mail: voronts@catalysis.ru

Received 23 July 2008
Uspekhi Khimii **77** (10) 973 – 991 (2008); translated by T Ya Safonova

transient interactions with reactants and are regenerated at the end of the reaction.

The rapid progress in the field of photocatalysis started in the 1980s -1990s as a consequence of the growing interest in economic ways of conducting reactions that in the case of classical catalysis proceed under severe conditions (*e.g.*, deep oxidation) or do not proceed at all (*e.g.*, water decomposition to oxygen and hydrogen). Photocatalytic reactions proceed as a rule at considerable rates at room temperature and ambient pressure. The growing attention to this field is reflected in the steadily increasing number of publications that exceeded 10 thousand in 2008.

The progress in the development of photocatalysis was surveyed in several reviews that considered the state of the art in the field of heterogeneous catalysis in the mid-1990s,[6,7] gave a detailed description of studies on photocatalysis on titanium dioxide, including the data up to 2004 (Ref. 8) and dwelled into the mechanism of surface phenomena that accompany photocatalysis on TiO_2.[9] The field of heterogeneous photocatalysis on titanium dioxide embraces several thousand publications. Obviously, such general reviews can hardly contain sufficient information on the progress in studies dealing with transformations of particular classes of chemical compounds.

In the present review, the reactions of organic sulfur compounds and H_2S that involve heterogeneous and homogeneous photocatalysts in the liquid and gas phases are considered. Attention is focused on reduced sulfur compounds.

Photocatalytic transformations of sulfur compounds attract keen attention of scientists in the fields of both photochemistry and physical organic chemistry and also applied environmental sciences. The low ionisation potential of sulfur compounds makes it possible to use photocatalysis for generation of radical cations for investigation of their subsequent transformations that play an important role in biochemical processes. Many of pesticides, chemical warfare agents (CWA), malodorous and toxic substances, detergents are sulfur compounds. Photocatalytic processes are of practical interest for the efficient decomposition of these compounds, particularly, under the action of sunlight.

Organic sulfur compounds play a dual role in the life of modern society. The development of efficient pesticides is of great importance for increasing the crops production. Many reduced sulfur compounds were used in organic synthesis as inhibitors of biocorrosion, additives for rubber vulcanisation, odorants in inflammable gases and also as radioprotectors. At the same time, the reduced sulfur compounds often present a severe problem and need to be removed and decomposed. A typical example is the undesired foul sulfur-containing products of organic waste biodegradation. Toxic sulfur-containing pesticides pollute water in many districts. Certain of reduced sulfur compounds are extremely toxic warfare agents. Finally, the removal of sulfur compounds to a level below 1 ppm is a challenge in the power industry.

Large amounts (tonnes) of sulfur compounds cannot be by photocatalytic oxidation methods because this would require a huge number of photons; at the same time, these methods are highly competitive for processing dilute streams of air and, probably, water containing low amounts of sulfur compounds.

Reduced sulfur compounds are also of interest for fundamental studies. Usually, it is assumed that the photocatalytic oxidation of organic and inorganic substances on TiO_2 is initiated by hydroxyl radicals. This is true for the cases where the water oxidation by light-generated 'holes' proceeds faster than the direct substrate oxidation. However, for certain substrates with low redox potentials, the direct oxidation by photogenerated 'holes' is possible. Organic sulfides are the typical reduced sulfur compounds. Their redox potential (E°) may be as low as $+1.7$ V (from hereon, the potentials are related to the normal hydrogen electrode).[10] This is much lower than the potential of water oxidation to hydroxyl radical ($E^\circ = 2.59-2.74$ V).[11] Thus, organic sulfides provide a unique opportunity for studying the reactions of direct oxidation with photogenerated 'holes'.

II. Classes of sulfur compounds studied in photocatalytic processes

Organic sulfur compounds studied so far in photocatalytic processes largely pertain to alkane- and arenethiols, aliphatic and aromatic sulfides (including halogen-substituted), sulfur-containing heteroaromatic compounds; pesticides form a special group. In this section, we consider the main characteristics of these classes of compounds and also their photocatalytic reactions.

Hydrogen sulfide and thiols have an extremely strong and foul odour. The odour detection limit is, *e.g.*, 0.4 ppb for H_2S, 0.07 ppb for MeSH and 3 ppb for Me_2S.[12] Due to this feature, thiols are used as the odorants of inflammable gases. Vertical ionisation potentials of aliphatic thiols are relatively low (for example, 9.44 eV for MeSH). The ionisation potential of H_2S is 10.5 eV.[13] The larger thiol molecules have lower ionisation potentials (9.31 eV for EtSH). At neutral pH, the standard redox potentials of thiols are approximately at -1.3 V.[14] The most typical chemical property of thiols is their ability to be easily oxidised to disulfides. The reaction proceeds most rapidly in alkaline media because RS^- anions are very easily oxidised, for instance, $E^\circ = -0.75$ V for the oxidation of an EtS^- anion to a thiyl radical $EtS^\bullet$ and $E^\circ = -1.3$ V for the oxidation of EtSH.[14] Thiyl radicals are dimerised to disulfide in the diffusion-controlled mode. The relatively low S–H bond energy ($\sim$360 kJ mol^{-1}) is responsible for the easy elimination of the hydrogen atom from thiols. Due to this property, thiols are good radical scavengers and are used as radioprotectors. Thiol dimerisation precedes the stages of photocatalytic oxidation.

Adiabatic ionisation potentials of aliphatic sulfides are still lower compared to thiols, namely, 8.7 eV for Me_2S, 8.42 eV for Et_2S and 8.20 eV for Pr^i_2S and $MeSCH{=}CH_2$ (NIST database †). Redox potentials of aliphatic sulfides can be detected only by fast methods, for example, pulse radiolysis, and are equal to -1.66 V for Me_2S and -1.63 V for Bu^t_2S (Ref. 10). The electrochemical method also allows one to oxidise aliphatic sulfides; however, it gives no way for determination of redox potentials, because the process is irreversible. It is assumed that the oxidation involves the formation of radical cations as intermediate products.

† The open database NIST is available in http://webbook.nist.gov/chemistry/ie-ser.html

Radical cations of organic sulfides can react with neutral molecules to form dimers of the σ-type with two-centred three-electron (2c, 3e) S–S bonds.[15]

$$R_2S^{+\bullet} + R_2S \longrightarrow [R_2S.\therefore SR_2]^+.$$

For aliphatic sulfides (R = Me, Et, Pr^n), the enthalpy of dimer formation (according to experimental data and results of calculations‡) was found to be 110–120 kJ mol^{-1}. Radical cations of aromatic sulfides, for example, MeSAr, form also π-type dimers.[15]

The appearance of dimers in photocatalytic reactions was studied so far only by the example of 4-methylbenzoic acid oxidation on TiO_2.[16] The dimer formation was confirmed by the following changes in the electron absorption spectrum of an intermediate as the substrate concentration varied from 1 to 10 mmol $litre^{-1}$: the absorption band intensity with the maximum at 730 nm increased much more profoundly that the band at 545 nm.

A sulfur atom of aliphatic sulfides can be oxidised to a sulfoxide group under the action of different oxidants and in photocatalytic reactions (Table 1). Photocatalytic reduction of sulfides leads to thiols and hydrocarbons.

Adiabatic ionisation potentials of aromatic sulfides containing phenyl substituents are sufficiently low (for example, 7.9 eV for Ph_2S). Ionisation of heteroaromatic compounds resulted in the loss of aromaticity; hence, their ionisation potentials are relatively high (8.9 eV for thiophene). Redox properties of aromatic sulfides were studied sufficiently thoroughly because they form relatively stable radical cations. Despite the great difference in the ionisation potentials of aromatic and aliphatic sulfides, the redox potentials of aromatic sulfides are only slightly lower (*e.g.*, for Ph_2S $E^\circ = -1.53$ V).

Chemical properties of aromatic thiols and sulfides closely resemble those of the corresponding aliphatic compounds. In heteroaromatic compounds, a sulfur atom is less reactive; however, they can also be oxidised to sulfoxides and sulfones, particularly, by a photocatalytic reaction. Table 2 shows reduced sulfur compounds containing aromatic fragments, which were studied in photochemical reactions.

From the viewpoint of practice, studying photocatalytic reactions of pesticides is of special interest (Table 3). Pesticides are substances used in the removal of interfering microorganisms, plants and animals. A special place among them is occupied by insecticides that act against insects largely by damaging their nervous system. Sulfur-containing insecticides include organophosphorus compounds (phosphorothioates and phosphorodithioates), carbamates and other compounds with sulfur in the sulfide form. Organophosphorous insecticides are very toxic for people. Thus the lethal dose (LD_{50}) of Parathion is 6–50 mg kg^{-1}. Carbamates can be even more toxic.

Among compound shown in Table 3, a sulfur-containing herbicide Irgarol is present. It suppresses photosynthesis and due to its low toxicity for animals and low solubility in water is used for inhibiting the growth of algae on surfaces immersed in water.

At room temperature, pesticides usually represent solid crystalline substances or thick liquids with boiling points above 200 °C. As a rule, they are poorly soluble in water but dissolve in organic solvents. When developing pesticides, attention was focused on their outdoor stability. It is for this reason that the water pollution with pesticides has become such a serious problem which is difficult to solve by biological methods.

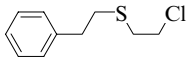
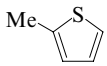
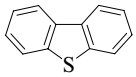
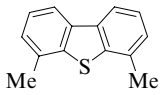
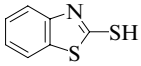
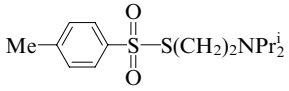
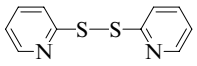
Table 1. Studied photocatalytic transformations of aliphatic sulfur compounds and H_2S.

Substrate	System, photocatalyst	Ref.
H_2S	air, TiO_2	17–21
	air, TiO_2–ZrO_2	20
	air, Ag–TiO_2	22
	H_2O, CdS/TiO_2	23, 24
	propene, TiO_2	25
MeSH	air, Ag–TiO_2	22
	TiO_2	26, 27
EtSH	air, TiO_2	28
Me_2S	air, TiO_2	29–32
	air, S–TiO_2	33
	air, DCA/SiO_2	34–36
	air, ANT/SiO_2	34, 36
	air, TiO_2/SiO_2	37
Me_2S_2	air, TiO_2	32, 37, 38
	air, TiO_2, ZnO	39
Et_2S	air, TiO_2	40–43
	TiO_2/SiO_2	44
	C_6H_6, TPP	45
	MeCN, DCA	46
$MeS(CH_2)_2Cl$	MeCN, TiO_2	47
$EtS(CH_2)_2Cl$	MeCN, TiO_2	47
	air, TiO_2	48, 49
	TiO_2/SiO_2	44, 50, 51
	sulfated TiO_2	52
$(ClCH_2CH_2)_2S$	MeCN, TiO_2	53
(Yperite)	air, TiO_2	54
Bu^n_2S	MeCN, DCA/SiO_2	55
	MeCN, TiO_2	56
	MeCN, DCA/SiO_2	57
	MeCN, DCA, NMQ^+	58
$Bu^n_2S_2$	MeCN, DCA/SiO_2	57
Bu^t_2S	MeCN, TiO_2	56
$(n\text{-}C_6H_{13})_2S$	MeCN, TiO_2	56
	air, TiO_2	38
	TiO_2	38
$HS(CH_2)_2NHBu^n$	H_2O, TiO_2	59, 60

Note. From hereon, the following designations are taken: DCA is 9,10-dicyanoanthracene, ANT is 9,10-anthraquinone, TPP is tetraphenylporphyrin, NMQ^+ is *N*-methylquinolinium tetrafluoroborate.

‡ M A James, A J Illies *J. Phys. Chem.* **100** 15794 (1996)

Table 2. Studied photocatalytic reactions of sulfur compounds containing aromatic fragments.

Substrate	System, photocatalyst	Ref.	Substrate	System, photocatalyst	Ref.
Ph_2S	MeCN, DCA/SiO_2	55	$(4\text{-}RC_6H_4CH_2)_2S$	MeCN, TiO_2	63
	MeCN, TiO_2	56, 61	R = H, Me, OMe, Cl, Br		
	MeCN – H_2O, TiO_2	62		H_2O, TiO_2	70
$(4\text{-}XC_6H_4)_2S$	MeCN, TiO_2	63		air, TiO_2	70
X = H, Me, OMe, Cl, Br				air, TiO_2	38
					
R = Y = H: X = H, OMe; X = R = H, Y = OMe	MeCN, TiO_2	61		CH_2Cl_2 – H_2O, TiO_2	71
R = Y = H: X = H, OMe; X = Y = H, R = Me	MeCN, DCA	64		MeCN, $FePc/SiO_2$	72
X = Y = R = H	MeCN, TiO_2	61			
	MeCN, TNM	65		MeCN, TiO_2	73, 74
	MeCN – H_2O, TiO_2	62		PhMe, POM	75
				$C_{14}H_{30}$, TiO_2	76
				MeCN, TiO_2	74
R = H, Ph; X = $SiMe_3$, CO_2H	MeCN, NMQ^+, DCN, TP, TCB	66			
$4\text{-}RC_6H_4SMe$				H_2O, TiO_2	77
R = H	MeCN, DCA or NMQ^+	58		H_2O, La – TiO_2	78
	MeCN, TNM	65			
	MeCN – H_2O, TiO_2	62			
R = H, Me, OMe, Et, F, Cl	MeCN or MeOH, TiO_2	67, 68		MeCN, TiO_2	79
R = OH, CH_2CO_2H, CH_2OH, Me	TiO_2/CM-β-CD	69	(simulant of VX CWA)		
				MeCN – H_2O, TiO_2	80
$Ph(CH_2)_2SPh$	MeCN, TiO_2	61			

Note. The following designations are taken: TNM is tetranitromethane, DCN is 1,4-dicyanonaphthalene, TP is triphenylpyrylium tetrafluoroborate, TCB is 1,2,4,5-tetracyanobenzene, CM-β-CD is carboxymethyl-β-cyclodextrin, FePc is iron phthalocyanine, POM are polyoxometallates.

Table 3. The main studied photocatalytic reactions of sulfur-containing pesticides.

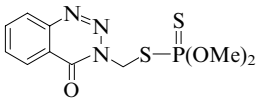
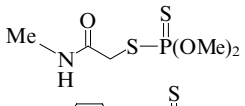
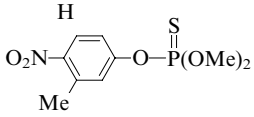
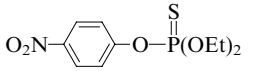
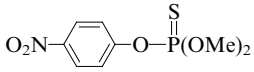
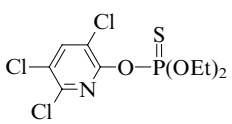
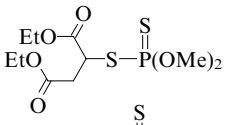
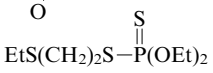
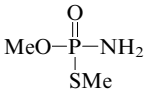
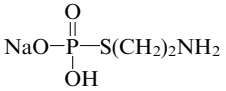
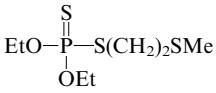
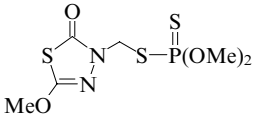
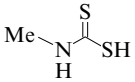
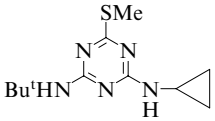
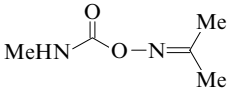
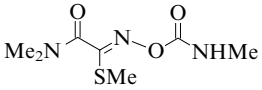
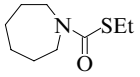
Structural formula	Commercial name	System, photocatalyst	Ref.
	Methylazinphos	H_2O, TiO_2	81
		Fe^{III} – H_2O_2, UV	82
	Dimethoate	H_2O, TiO_2	81, 83 – 87
	Fenitrothion	H_2O, TiO_2	88, 89
		H_2O, TiO_2, $PW_{12}O_{40}^{3-}$	90, 91
	Parathion (ethylparathion)	H_2O, TiO_2	92 – 96
		anthracene/dextran	97
	Methylparathion	H_2O, TiO_2, ZnO	98, 99
		$H_3PW_{12}O_{40}/TiO_2$	100
		$H_6P_2W_{18}O_{62}/TiO_2$	100
		H_2O, ZnS/TiO_2	101
		H_2O, Bi^{3+}/TiO_2	102
		TPP/Y-zeolite	103
	Chloropyriphos	H_2O	104

Table 3 (continued).

Structural formula	Commercial name	System, photocatalyst	Ref.
	Malathion	H_2O, TiO_2	105
	Disulfoton	H_2O – MeCN, TiO_2	106
	Methamidophos	H_2O, TiO_2	107
	Cysteamine-*S*-phosphate	H_2O, TiO_2	108
	Phorate	H_2O, TiO_2	92, 93, 109
	Methidathion	H_2O, TiO_2	110
	Vapam	H_2O, TiO_2	111
	Irgalol	H_2O, TiO_2	112
	Methomyl	H_2O, TiO_2	85, 86, 113, 114
	Oxamyl	H_2O, TiO_2	85, 86, 115, 116
	Molinate	H_2O, TiO_2	117

III. Products of photocatalytic reactions

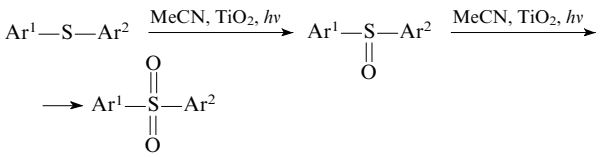
Photocatalytic reactions of sulfur compounds were carried out in the gas or liquid phases. Aromatic compounds were used exclusively in their dissolved form, whereas nearly a half of all studies of aliphatic compounds were conducted in the gas phase or at the gas–solid interface. This was associated with the low volatility of aromatic sulfur compounds and a sufficiently high vapour pressure of aliphatic compounds. The set of products formed in photocatalytic reactions strongly depended on both the structure of sulfur compounds and the reaction conditions.

1. Aromatic sulfur compounds

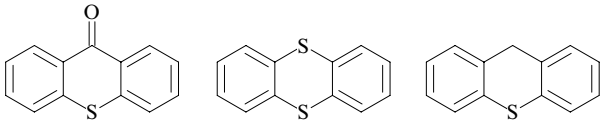
Strictly speaking, this group of compounds should include only those compounds that contain a sulfur atom bound to at least one aromatic substituent or is a part of an aromatic ring. However, for the sake of convenience, this Section also includes the data on certain di(phenylalkyl) sulfides (*e.g.*, for dibenzyl sulfide).

In earlier studies, carrying out a photocatalytic reaction involved the use of a titanium dioxide suspension in oxygen-saturated acetonitrile.[56] The product composition depended on the irradiation time, because the photocatalytic oxidation products could be oxidised further up to inorganic substances. However, their complete oxidation in acetonitrile has never been reported.

As a rule, oxidation of aromatic sulfides proceeded at the sulfur atom to gradually yield sulfoxides and sulfones.[61, 63]

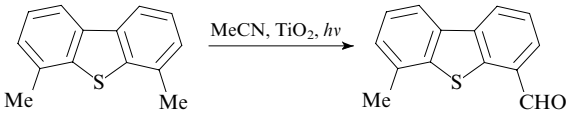


This reaction is also typical of sulfur-containing heteroaromatic compounds. Thus dibenzothiophene underwent the oxidation of its sulfur atom to form sulfoxide or sulfone as the main reaction products.[73, 74] The same products were observed at photooxidation of thioxanthone and thianthrene.[73] In the latter case, two sulfur atoms involved in the central ring successively underwent oxidation to form sulfoxide or sulfone groups. In a thioxanthene molecule, the oxidation under the same conditions involved not only a sulfur atom but also CH_2 groups in the central ring. As a result, the basic products were the same as in the thioxanthone oxidation.



Thioxanthone Thianthrene Thioxanthene

Introduction of substituents into aromatic rings may give rise to a changeover of the oxidation target. For instance, in 4,6-dimethyldibenzothiophene, only one of two methyl groups was oxidised to form the corresponding aldehyde.[74]



Methylaryl sulfides (*e.g.*, methylphenyl sulfide) were oxidised at a sulfur atom to yield sulfoxide and sulfone as the main products.[67]

Introduction of a CH_2 group between the sulfur atom and an aromatic substituent changed the composition of reaction products. In oxygen-saturated acetonitrile suspensions of titanium dioxide, under UV radiation, dibenzyl sulfides largely underwent the sulfur–carbon bond cleavage.[63]

$$(4\text{-}XC_6H_4CH_2)_2S \xrightarrow{MeCN,\ TiO_2,\ h\nu} 4\text{-}XC_6H_4CHO + \ldots$$

X = H, Me, OMe, Cl, Br.

As a rule, asymmetrical sulfides containing a phenyl and a phenylalkyl groups were also oxidised with the C–S bond cleavage. For the most part, the sulfur atom in products remained attached to the phenyl group.[61]

$$4\text{-}MeOC_6H_4CH_2SPh \xrightarrow{MeCN,\ TiO_2,\ h\nu} 4\text{-}MeOC_6H_4CHO + \ldots$$

The oxidation of the corresponding sulfoxide (4-methoxybenzyl phenyl sulfoxide) also led to the C–S bond cleavage on the side of the phenylalkyl substituent. The introduction of longer alkyl chains into a phenyl phenylalkyl sulfide did not change the main direction of the photocatalytic reaction. Thus the main reaction pathway was the C–S bond cleavage at the phenetyl group in phenetyl phenyl sulfide. This included the formation of a considerable amount of sulfoxide.[61]

$$PhCH_2CH_2SPh \xrightarrow{MeCN,\ TiO_2,\ h\nu} PhCH_2CHO + \ldots$$

Organic sensitisers in their dissolved or heterogenised states were often used as homogeneous photocatalysts. Like titanium dioxide, they reacted with the substrate and, upon the absorption of light quanta, induced chemical transformations. For example, 9,10-dicyano anthracene was used in the oxidation of several organic sulfur compounds to form products similar to those yielded by photocatalysis with titanium dioxide.

Thus the oxidation of benzyl phenyl sulfides in deuterated acetonitrile led to the corresponding benzaldehydes. A considerable amount of deuterated benzylacetamide was formed,[64] which pointed to a reaction with the solvent.

$$4\text{-}XC_6H_4CH_2SPh \xrightarrow{CD_3CN,\ DCA,\ h\nu} 4\text{-}XC_6H_4CHO + 4\text{-}XC_6H_4CH_2NHC(O)CD_3 + \ldots$$

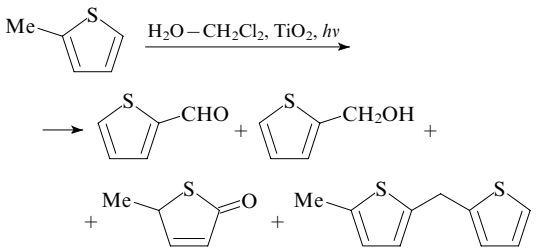
X = H, OMe.

If the sulfur atom was bound to a quaternary carbon atom, the chief oxidation route was also the C–S bond cleavage. For example, oxidation of phenyl 2-phenylprop-2-yl sulfide yielded 2-phenylpropan-2-ol as the main product, while methylstyrene and acetophenone were formed in smaller amounts; no reaction products with acetonitrile were detected in this case.

$$PhCMe_2SPh \xrightarrow{CD_3CN,\ DCA,\ h\nu} PhCMe_2OH + PhC(Me){=}CH_2 + PhC(O)Me$$

Thus, photocatalytic oxidation of reduced sulfur compounds in acetonitrile followed the three main routes: oxidation of a sulfur atom to the sulfoxide or sulfone groups, cleavage of a C–S bond to form an alcohol or an aldehyde and the oxidation of carbon atoms unconnected directly with the sulfur atom.

Photocatalytic reactions of organic sulfur compounds in aqueous or mixed water-organic solutions usually led to a greater diversity of products as compared with reactions in pure acetonitrile. For example, methylthiophene was oxidised in a TiO_2 suspension,[71] where a mixture of water and dichloromethane (1 : 1) was used as the solvent because methylthiophene is insoluble in pure water. Among the reaction products, aldehydes, alcohols and also methylthiophene dimers and trimers were detected.



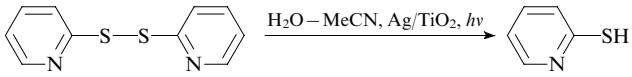
Aqueous solutions are suitable for carrying out photocatalytic reactions of water-soluble organic sulfur compounds. Such compounds should contain highly polar groups or form them in the course of dissolution prior to the beginning of a photocatalytic reaction. For example, during the dissolution, 2-phenetyl 2-chloroethyl sulfide (PECES) underwent hydrolysis.[70]

$$Ph(CH_2)_2S(CH_2)_2Cl \xrightarrow{H_2O} Ph(CH_2)_2S(CH_2)_2OH.$$

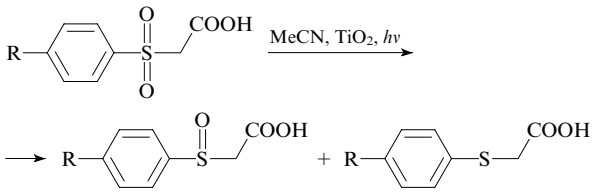
Photocatalytic reactions of 2-hydroxyethyl 2-phenetyl sulfide (HEPES) led to the preferential break of a C—S bond. Styrene was the main reaction product; benzaldehyde and 2-phenethylsulfonic acid were also formed, albeit in much smaller amounts, together with numerous less important products. It should be noted that neither sulfoxide nor sulfone were found in reaction products.

$$Ph(CH_2)_2S(CH_2)_2OH \xrightarrow{H_2O,\ TiO_2,\ h\nu} PhCH{=}CH_2 + PhCHO + Ph(CH_2)_2SO_3H.$$

The use of pure and metallised TiO_2 allowed not only the oxidation but also the photochemical reduction of sulfur compounds to be conducted. Thus on an Ag/TiO_2 catalyst under anaerobic conditions, the photocatalytic reduction of disulfide to the corresponding thiol was carried out.[80]



The reduction of a series of arylsulfonylacetic acids on titanium dioxide in methanol led to the corresponding sulfoxides and sulfides, where the sulfoxide yield increased as the donor properties of the R substituent were enhanced.[118]



R = H, Me, OMe, F, Cl, Br.

2. Aliphatic compounds of sulfur and H_2S

Transformations of aliphatic sulfur compounds and H_2S were studied in both dissolved state and the gas phase. An HS^- ion is a good electron donor and readily undergoes oxidation in water even in the presence of narrow band gap photocatalysts. In the absence of oxygen, water was reduced by electrons to yield gaseous hydrogen.[23,24] Thus water was cleaned and valuable fuel was produced simultaneously.

The photocatalytic oxidation of hydrogen sulfide in the gas phase can be used for its removal from air. As the intermediate oxidation product, adsorbed SO_2 was detected.[19] The final product of the H_2S photocatalytic oxidation on titanium dioxide was sulfuric acid adsorbed on the photocatalyst surface.[17–21] To accelerate this reaction, one can modify titanium dioxide with metals. Addition of silver resulted in an increase in the hydrogen sulfide adsorption and a sevenfold increase in its oxidation rate.[22]

Photocatalytic transformations can be used in the gas-phase organic synthesis. Thus hydrogen sulfide addition to propene on the surface of irradiated titanium dioxide yielded propane-1-thiol.[25]

Methane- and ethanethiol are low-boiling compounds. Their photocatalytic oxidation was studied in the gas phase. Photocatalytic oxidation of ethanethiol produced the following gaseous products: SO_2, AcOH, CO and CO_2. No analysis of the surface reaction products was carried out.[28]

Several studies were devoted to the photocatalytic oxidation of the simplest organic sulfide, namely, dimethyl sulfide. The gaseous and adsorbed products of its oxidation on titanium dioxide were studied in detail.[30] In the gas phase, dimethyl disulfide, sulfur dioxide and carbon dioxide were detected. On the titanium dioxide surface, dimethyl sulfoxide, dimethyl sulfone, methanesulfonic and sulfuric acids were found.

$$Me_2S \xrightarrow{O_2,\ TiO_2,\ h\nu} Me_2SO(ads) + Me_2SO_2(ads) + Me_2S_2(gas) + SO_2(gas) + CO_2(gas) + H_2SO_4(ads) + MeSO_3H(ads).$$

The presence of these products suggests that the reaction followed two main routes, namely, the sulfur oxidation and the carbon—sulfur bond cleavage. The product yielded by the C—S bond cleavage (dimethyl disulfide)[30,33] was detected in an amount roughly equal to the total quantity of dimethyl sulfoxide and dimethyl sulfone. Thus, the sulfur atom oxidation and the carbon—sulfur bond cleavage played equal roles in this reaction.

When a silica gel-fixed organic sensitiser (anthraquinone or dicyanoanthracene) served as the photocatalyst, the products preferentially detected in the gas phase and on the photocatalyst surface were due to the incomplete oxidation.[34,36]

$$Me_2S \xrightarrow{O_2,\ ANT,\ h\nu} Me_2SO + Me_2SO_2 + Me_2S_2 + Me_2S_3 + MeSCH_2SMe + HCHO + MeSH + MeS(O)_2SMe.$$

For the most part, dimethyl sulfoxide, dimethyl sulfone and dimethyl disulfide were formed, *i.e.*, the main products were the same as in photocatalytic reactions on TiO_2. Probably, the oxidation mechanisms on both types of photocatalysts are similar. Substantial differences in the yields of the Me_2S photocatalytic oxidation products formed on titanium dioxide and DCA were revealed.[35] On TiO_2, deep oxidation products, namely, dimethyl disulfide and trisulfide, prevailed, whereas on DCA, larger amounts of sulfone and sulfoxide were formed. This difference may suggest that the oxidation on DCA involves singlet oxygen.

Photocatalytic oxidation of diethyl sulfide vapour on TiO_2 was studied in detail.[40–44] The distribution of oxidation products depended on the air humidity, the light intensity, the time of contact with the catalyst, the catalyst mass and also on the time passed from the reaction beginning to the photocatalyst deactivation.[41,42] The main gaseous intermediate products were diethyl disulfide, ethylene, acetaldehyde, acetic acid and SO_2. The main surface intermediate products were diethyl trisulfide, diethyl sulfoxide and ethanesulfonic acid.

$$Et_2S \xrightarrow{O_2,\ TiO_2,\ h\nu} Et_2S_2(ads) + Et_2S_3(ads) + CH_2{=}CH_2(gas) + SO_2(gas) + MeCHO(gas) + MeCO_2H(gas) + Et_2SO(ads) + EtSO_3H(ads) + CO_2(gas) + H_2SO_4(ads).$$

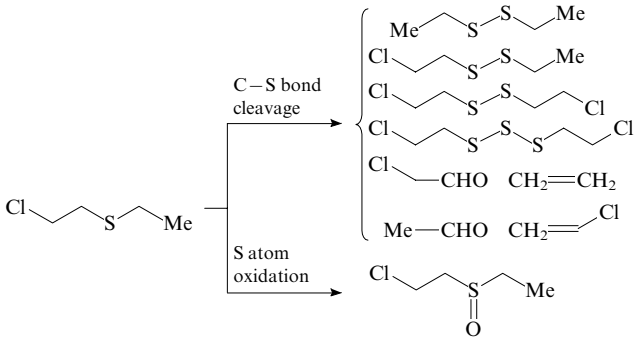
The reaction products resembled those obtained in dimethyl sulfide oxidation. The only difference concerned the formation of ethylene from diethyl sulfide, which is impossible in the case of dimethyl sulfide.

Transformations of chlorine-containing aliphatic sulfides were studied by the example of 2-chloroethyl sulfides. These substances are poorly soluble in water; hence, their

photocatalytic oxidation was carried out in acetonitrile, acetonitrile–water mixtures and in the gas phase. Oxidation in acetonitrile on irradiated TiO_2 yielded the corresponding sulfoxides and sulfones.[47] However, no attempts to find more volatile products such as ethylene, chloroethylene, acetaldehyde, *etc*. were undertaken in this study. Hence, it is very likely that in this case, the preferential reaction channel could be the carbon–sulfur bond cleavage. The oxidation of methyl 2-chloroethyl sulfide produced different disulfides, namely, Me_2S_2, $MeS_2(CH_2)_2Cl$, $(ClCH_2CH_2)_2S_2$.[53] In the oxidation in a H_2O–MeCN mixture, as a result of the hydrolysis of 2-chloroethyl ethyl sulfide (CEES) and methyl 2-chloroethyl sulfide, the corresponding 2-hydroxyethyl sulfides were formed. In addition to sulfoxide and sulfone, the oxidation yielded other unidentified reaction products.

In the gas-phase photocatalytic oxidation of CEES, water present on the TiO_2 surface caused the hydrolysis to yield 2-hydroxyethyl ethyl sulfide. However, a substantial amount of nonhydrolysed CEES also took part in photocatalytic reactions, as follows from the composition of detected products (Scheme 1).[48,49] Insofar as a CEES molecule contains two different alkyl radicals at the sulfur atom, the cleavage of C–S bonds led to two sets of products. Thus, ethylene and chloroethylene, acetaldehyde and chloroacetaldehyde and also SO_2 were present in gaseous intermediate products, while diethyl disulfide, 2-chloroethyl ethyl disulfide, bis(2-chloroethyl) disulfide and chloroethyl ethyl sulfoxide were the main intermediate products extracted from the photocatalyst surface.

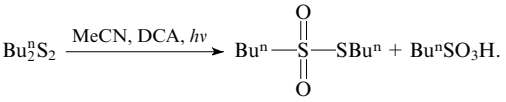
Scheme 1



The photocatalytic oxidation of yperite in a TiO_2 suspension in acetonitrile was studied aimed at elucidating the prospects of its use in decontamination.[53] As the main products, yperite sulfoxide $[ClCH_2CH_2S(O)CH_2CH_2Cl]$ and yperite disulfide $(ClCH_2CH_2SSCH_2CH_2Cl)$ were detected. It was noted that direct photolysis proceeded faster than photocatalytic oxidation. The same conclusion was drawn when studying the yperite photolysis and photocatalytic oxidation in the gas phase.[54] Among all CWA studied, only yperite demonstrated the higher photolysis rate as compared with photocatalytic oxidation. However, photolysis can produce equally toxic nonvolatile products, and detoxication is not achieved.

Reactions of dibutyl sulfide and dibutyl disulfide were studied on pure and silica gel-grafted photosensitisers in oxygen-saturated acetonitrile.[55–57] Dibutyl sulfoxide was the main product of dibutyl sulfide transformations. In addition, small amounts of dibutyl sulfone and dibutyl disulfide were detected.

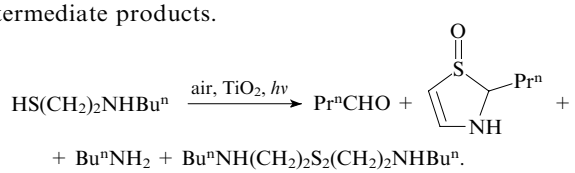
The formation of disulfide occurs due to the C–S bond cleavage. The photocatalytic reaction of dibutyl disulfide on grafted DCA preferentially yielded dibutyl thiosulfonate and butanesulfonic acid.



Gas-phase photocatalytic reactions may follow an entirely different pathway as compared with liquid-phase reactions. Non-volatile compounds cannot leave the photocatalyst surface by any other way except for being transformed into more volatile products. At the same time, at deep oxidation, the organic compounds of reduced sulfur can be transformed to polar oxidation products and, eventually, H_2SO_4. In a series of successive sulfur oxidation products, only SO_2 was highly volatile and capable of leaving the catalyst surface at room temperature. The other products were accumulated on the photocatalyst surface. Adsorbed products limited the accessibility of reaction sites for further reaction; hence, the photocatalyst deactivation was inevitable after a certain amount of sulfur had been transformed. Despite deactivation, the gas-phase photocatalysis is more attractive for practice, because the quantum yield of gas-phase reactions often exceeds that of analogous liquid-phase reactions by an order of magnitude.

Thus photocatalytic oxidation of PECES on TiO_2 proceeded with the considerably higher quantum yield as compared with the liquid phase;[70] however, styrene was still the only oxidation product. For the gas-phase reaction, this product was totally localised on the photocatalyst surface.

The presence of other heretoatoms in the organosulfur compound to be oxidised severely complicated the composition of reaction products. Photocatalytic oxidation of 2-(butylamino)ethanethiol (BAET) in an aqueous TiO_2 suspension produced more than 30 intermediates.[59] The final oxidation products were CO_2 and ammonium sulfate. The following reaction scheme demonstrates the main intermediate products.

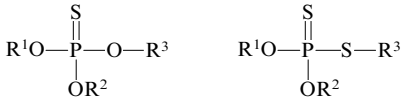


$$+ Bu^nNH_2 + Bu^nNH(CH_2)_2S_2(CH_2)_2NHBu^n.$$

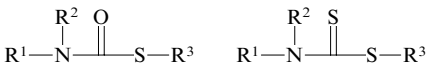
Dimerisation of the original thiol to form disulfide occurred before this reaction started. The further transformations produced linear and cyclic products among which 2-propyldihydrothiazole *S*-oxide prevailed.

3. Pesticides

Cleaning water from pesticides is a very important problem, because these compounds are highly toxic and widely used in agriculture. Hence, a fairly large number of studies were devoted to the photocatalytic water cleaning from dissolved pesticides. Sulfur-containing pesticides may be represented by the following basic classes:



Phosphorothioates Phosphorodithioates

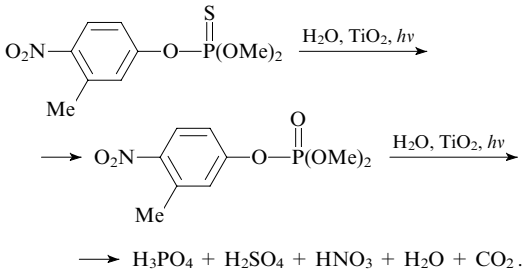


Thiocarbamates Dithiocarbamates

Some pesticides contain a sulfide group, for example, prometryne [119] and irgarol [112] (see Table 3) contain a methyl sulfide group attached to a triazine ring. Photocatalytic oxidation of these compounds usually involves sulfur atom oxidation to a sulfoxide or sulfone group. Further reactions of sulfones follow pathways described in the previous sections of this chapter. Additional reaction pathways are due to the presence of a triazine ring and substituents therein.

Sulfur-containing pesticides shown above represent fundamentally new classes of compounds. Phosphorothioates contain a P=S bond, phorphorodithioates include a S−P=S group, and thiocarbamates and dithiocarbamates contain the N−C−S and N−CS_2 moieties, respectively.

Photocatalytic oxidation of phosphorothioates in an aqueous TiO_2 suspension produced the corresponding phosphate as the main intermediate, *i.e.*, the sulfur atom oxidation and its displacement by an oxygen atom took place. Further oxidation resulted in complete mineralisation, *i.e.*, the formation of carbon dioxide, water and inorganic acids, namely, sulfuric, nitric, nitrous and phosphoric. The photocatalytic oxidation of phosphorothioates was demonstrated by the example of fenitrothion, an insecticide.[90]

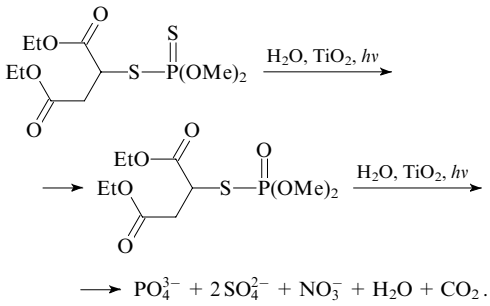


Simultaneously with the sulfur atom oxidation to form fenitrooxon, the oxidation of a methyl group attached to the benzene ring may proceed to form formylfenitrothion. With a homogeneous photocatalyst $H_3PW_{12}O_{40}$, analogous intermediates were formed and complete mineralisation of fenitrothion could also be achieved.

Analogous reactions were studied for methylparathion [98] and parathion.[96,97] The preferential oxidation of the sulfur atom was confirmed by the increase in the paraoxon concentration [96,98] and the fact that in kinetic curves, the sulfate concentration reached a plateau sooner than the phosphate concentration.[99] Using mass spectrometry, intermediates containing a sulfur atom were also found, namely, *O*,*O*,*O*- and *O*,*O*,*S*-trimethyl phosphorothioates. In addition, in parallel with paraoxon, *p*-nitrophenol was formed. Moreover, the attainment of a plateau by the sulfate concentration substantially lagged behind the paraoxon formation and the initial paraoxon consumption.[98] Hence, there exists an initial route of parathion transformation, alternative to the sulfur atom oxidation, in which sulfates are formed not from parathion but from a certain intermediate inorganic sulfur compound, *e.g.*, from sulfites. By measuring bioluminescence of *Vibrio fischeri* and the activity of *Daphnia magna*, it was shown that the photocatalytic oxidation led to a decrease in the reaction mixture toxicity.[96]

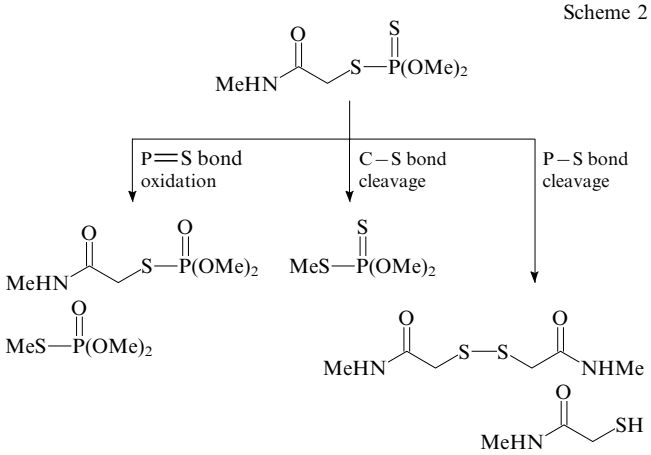
Photocatalytic oxidation of phosphorodithioates was studied for several insecticides (azinphos methyl, dimethoate, malathion, disulfoton, phorate and methidathion, see Table 3). The intermediate oxidation products were detected only in several studies.

The simplest situation was observed for malathion that contains no easily oxidisable atoms in the substituent at its sulfur atom. Its oxidation yielded malaoxon that is oxidised further to inorganic substances.[105] The detected intermediate products also included *O*,*O*,*S*-trimethyl phosphorothioate, diethyl methyl sulfonylsuccinate, several organic acids and their esters.



Sulfur-containing products of dimethoate photocatalytic reactions were studied in more detail. Based on the results obtained in Ref. 84, a scheme of initial pathways of photocatalytic reactions of this substance can be drawn (Scheme 2). The first channel leads to the substitution of the P=O group for the P=S group to form dimethoxon (omethoate). By the second and third channels, the cleavage of the sulfur−carbon or phosphorus−sulfur bond occurs. The corresponding products were identified by gas chromatography–mass spectrometry.

Scheme 2



The preferential cleavage of the phosphorus−sulfur bond was revealed at the photocatalytic oxidation of a model substance, cysteamine-*S*-phosphate (see Table 3).[108] It was found that the original substrate concentration decreases simultaneously with the increase in the phosphate ion concentration. Hence, the P−S bond cleavage is the first stage of oxidation of this substance and, probably, other analogous substances in the photocatalytic oxidation of phosphorothioates and phosphorodithioates.

Pesticides that belong to thiocarbamates and dithiocarbamates are represented in Table 3 by vapam, methomyl, oxamyl and molinate. In addition to reactions at sulfur atoms, the photocatalytic destruction channels involve the cleavage of bonds with nitrogen atoms. Thus the photo-

catalytic oxidation of methomyl yielded products corresponding to the cleavage of C–S (acetamide and acetonitrile) and N–C bonds and also to the hydrolysis of an N–O bond (methomyloxime).[113]

Photocatalytic oxidation of molinate that contains a nitrogen atom in the carbon ring (see Table 3) led to products that could be formed by the following routes: oxidation of a sulfur atom (molinate sulfoxide), oxidation of carbon atoms in the α-position with respect to the nitrogen atom (ketone), cleavage of a sulfur–carbon bond (thiols), cleavage of a nitrogen–carbon bond (hexahydroazepine).[117] Different carboxylic acids were also detected. A wide diversity of products and reaction pathways was associated with the presence of two or more electron donor atoms, namely, nitrogen and sulfur. The deep oxidation of a sulfur atom was completed much sooner than the oxidation of nitrogen and carbon atoms.

IV. Kinetics of photocatalytic oxidation

1. Mechanisms of photocatalytic reactions

The fundamental difference of photocatalytic reactions from other catalytic reactions lies in the fact that in the former, light quanta act as a reactant. This is why in addition to reaction conditions and the reactant and catalyst concentrations, one has to take into account the intensity of incident or absorbed light. The reaction mechanism differs from the mechanisms of common catalytic reactions because a photocatalyst (PC) absorbs light quanta to pass into an excited state.

$$PC + h\nu \longrightarrow PC^{**}.$$

An electronically excited state usually has a short lifetime and can undergo radiative or non-radiative transitions into the ground state or another excited state with lower energy (*i.e.*, more stable).

$$PC^{**} \longrightarrow \begin{cases} PC + (h\nu \text{ or } Q) \\ PC^{*} + (h\nu \text{ or } Q) \end{cases}$$

Q is the thermal energy.

Thus, 9,10-dicyanoanthracene excited by light with the wavelength $\lambda < 425$ nm passed to the singlet state ^{1}(DCA) and the latter transformed into the triplet state ^{3}(DCA) with the characteristic time of 11–15 ns and the quantum yield of 0.23 (see Ref. 120).

Similar processes in photocatalysis on semiconductors correspond to the formation of an electron–hole pair and the stabilisation (trapping) of these charge carriers on defects.

$$PC \xrightarrow{h\nu} PC + h^+ + e^-,$$
$$h^+ \longrightarrow h_t^+,$$
$$e^- \longrightarrow e_t^-,$$

where h_t^+ and e_t^- designate the trapped charge carriers. A photocatalyst in the excited state has a high redox potential. Thus 'holes' in TiO_2 had a potential of $\sim +3$ V,[121] whereas for ^{1}(NMQ)$^+$, $E^\circ = +2.7$ V.[58] These potentials substantially exceed the redox potentials of sulfur compounds (see Section II). Thus, the direct oxidation of sulfur compounds to form radical cations is possible.

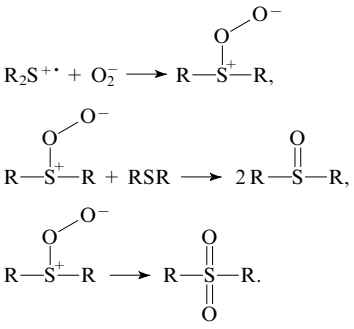
$$R_2S + h_t^+ \longrightarrow R_2S^{+\bullet},$$
$$R_2S + {}^1(NMQ)^+ \longrightarrow R_2S^{+\bullet} + NMQ.$$

Electrons in a semiconductor or reduced photocatalyst molecules could later react with the molecular oxygen present in the system.[57, 58]

$$e_t^- + O_2 \longrightarrow O_2^{-\bullet},$$
$$NMQ + O_2 \longrightarrow NMQ^+ + O_2^{-\bullet}.$$

Radical cations of sulfur compounds the formation of which was assumed back in 1983 (Ref. 56) were so far reliably detected only for aromatic compounds[68, 69, 122] and, probably, dibutyl sulfide.[58] This is associated with the longer lifetime of aromatic radical cations at room temperature (microseconds) and their easily recordable electronic absorption spectra with the peak at 500–550 nm. However, indirect data suggest that photocatalytic reactions of aliphatic sulfur compounds also proceed with the involvement of radical cations.

Mechanisms of reactions of radical cations of sulfur compounds can be elucidated by studying the distribution of photocatalytic reaction products. According to sets of reaction products of aromatic and aliphatic sulfides, which were discussed in Section III, a radical cation can undergo several types of transformations. The first type are oxidation reactions at the sulfur atom.[57, 123]



The second radical cation reaction type is the cleavage of a C–S bond. This reaction occurred if a sufficiently stable cationic fragment, *e.g.*, a benzyl cation, could be formed.[63]

$$[RSCH_2Ph]^{+\bullet} \longrightarrow RS^{\bullet} + PhCH_2^+.$$

The formed cation undergoes deprotonation and can later be transformed into an aldehyde.

$$RCH_2^+ \xrightarrow[-H^+]{} RCH^{\bullet} \xrightarrow{[O]} RCHO.$$

Sometimes, the products also contained an alcohol, which suggests that the cation reacts with water by adding a hydroxyl group.[64] Thiyl radicals were dimerised to form disulfides.[41]

$$RS^{\bullet} + RS^{\bullet} \longrightarrow RSSR.$$

The third reaction type is associated with oxidation of carbon atoms of the substrate. Carbon atoms adjacent to sulfur atoms were oxidised after the radical cation protonation.[124] Apparently, the other carbon atoms were oxidised as a result of their reaction with hydroxyl radicals. It should be mentioned that the interactions with photocatalysts can profoundly modify the radical cation reaction routes, for instance, by changing the relative contributions

of the reactions of C—S bond cleavage and sulfur atom oxidation[46,65] or by changing the position of splitting of intricate radical cations to fragments.[79] Thus photocatalytic splitting of substituted dithianes in the presence of a homogeneous photocatalyst, benzophenone, took place in the reaction between a sulfur-containing radical cation and a negatively charged photocatalyst molecule, which led to efficient deprotonation of the radical cation.[125] An analogous nucleophilic reaction with TiO_2 probably leads to radical cation deprotonation, which, for example, resulted in the 'anomalous' evolution of ethylene from diethyl sulfide.[41,48]

$$MeCH_2^+ \xrightarrow[-H^+]{} CH_2{=}CH_2 .$$

2. Kinetic dependences of liquid-phase reactions

Liquid-phase oxidation of organic substances can proceed at a steady rate, because no catalyst deactivation is usually observed in the liquid phase. This makes studying the liquid-phase kinetics a relatively easy task. The kinetic studies were carried out in static and flow reactors. When reactions were conducted in a static system, the time dependence of the original substrate concentration was well described by first-order kinetics.[74,84,97,113,117] Among the studied photocatalysts, TiO_2 was the most active, $PW_{12}O_{40}^{3-}$ could be equally active under certain conditions, zinc oxide was less active.[99,126] Among titanium dioxide samples, the highest activity is exhibited by Degussa P25 TiO_2 (Ref. 60). Doping TiO_2 with metallic silver[80] or lanthanum(III) salts (see Ref. 78) accelerated the photocatalytic reactions of sulfur compounds.

Factors that determine the rate of liquid-phase photocatalytic reactions include the reaction mixture pH, the temperature, the solvent nature, the suspension or solution concentration, the concentration of dissolved oxygen, the initial concentrations of substrates and additives. Below, we consider some of these factors.

a. The effect of solution pH

Solution acidity has a strong effect on the rate of liquid-phase photocatalytic reactions in water and polar solvents. This effect is associated with protonation or deprotonation of either the oxidisable substrate and the surface or the photocatalyst molecules. Protonation changes the ionisation potential, the redox potential and the adsorption properties of the substrate. Presumably, for a photocatalytic reaction to occur, the substrate and the photocatalyst should approach one another to a distance of several Å. Hence, weakening of their electrostatic repulsion increases the reaction rate.

When the solution pH exceed the pK_a values of the photocatalyst and the substrate, the latter are in the deprotonated state. Under these conditions, for an uncharged deprotonated substrate, high reaction rates are usually reached. Thus the rate of photocatalytic reduction of bis(2-bipyridyl) disulfide increased with increasing pH and reached a plateau at pH > 8.[80] Mineralisation of methylparathion was substantially accelerated as the pH increased to 9.[98] The photocatalytic oxidation of methyl phenyl sulfide, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, *p*-tolylmercaptan on TiO_2 was the fastest at pH 8–9.[62,66–69,77] The reaction rate decreased for both the higher and lower pH. However, the photocatalytic oxidation of benzimidazol-2-yl methyl sulfide, benzimidazol-2-yl propyl sulfide and benzimidazol-2-yl propen-3-yl sulfide proceeded at the highest rates at pH ~ 6.[126]

The photocatalytic oxidation usually yields a large amount of intermediate products which include various acids. Hence, the solution pH decreased as the process went on.[89] Thus the photocatalytic destruction of a thiosulfonate containing an amino group stopped at a certain degree of transformation due to the amino-group protonation by the formed sulfonic acid.[79]

Another difficulty in making corrections for the pH effect was associated with the different pK_a of intermediate products of photocatalytic oxidation. They could have the lower pK_a compared to the original substrate so that the optimal pH of the product decomposition might be lower than the optimal pH of the original substrate oxidation. As the example of the complicated dependence of the oxidation rate on the solution pH, let us consider the photocatalytic oxidation of 2-(butylamino)ethanethiol in an aqueous suspension of Degussa P25 TiO_2. No oxidation occurred for the initial solution pH < 9. Apparently, this is associated with the protonation of the secondary amino group in BAET and the TiO_2 surface. A BAET solution with the concentration of 250 mg litre^{-1} had pH ~ 9, and the maximum rate of BAET mineralisation was observed precisely at this pH. The oxidation kinetics was studied for the initial pH 11. The total organic carbon (TOC) content was constant in the first 100 min of the reaction, *i.e.*, no complete oxidation was achieved in this period. Later, the complete oxidation proceeded at such a high rate that to the 250th min, the reaction reached the same TOC conversion as for the oxidation at the initial pH 9. Moreover, it was found that at the initial pH 11, larger amounts of intermediate products were formed. Whereas a BAET molecule exhibits slightly basic properties and is uncharged at pH 11, its oxidation products such as sulfonic, sulfinic and carboxylic acids are negatively charged. This is why they were repulsed from the negatively charged titanium dioxide surface and were not oxidised until the solution pH decreased.[60]

b. The effect of photocatalyst concentration

The oxidation rate increased with an increase in the photocatalyst concentration. For the TiO_2 concentration of 200–2500 mg litre^{-1}, the rate reached a plateau[77,99,126] or demonstrated a maximum at a concentration of 500 mg litre^{-1} (Ref. 60). The optimal concentration depended on the solvent nature and the type of used TiO_2. In nonaqueous solvents, the optimal TiO_2 concentration was higher than in water apparently due to the faster sedimentation of photocatalyst suspensions.[47] For the photocatalytic oxidation of methyl 2-chloroethyl sulfide and 2-chloroethyl ethyl sulfide in acetonitrile, the substrate consumption rates increased with an increase in the concentration of titanium dioxide suspensions up to 400 mg litre^{-1}. For the photocatalytic oxidation of certain thiols in aqueous solutions, the rate of substrate consumption reached a plateau as the Degussa P25 TiO_2 concentration exceeded 2500 mg litre^{-1} (Ref. 77). However, the photocatalytic decomposition of 2-(butylamino)ethanethiol proceeded at a the maximum rate when the concentration of the Degussa P25 TiO_2 photocatalyst suspension was 500 mg litre^{-1} (Ref. 60). For the photocatalytic decomposition of methylparathion, the initial rate increased and reached a plateau at the catalyst concentration in suspension ~200 mg litre^{-1} for TiO_2 and ~800 mg litre^{-1} when

zinc oxide was used as the photocatalyst.[99] Such a wide scatter in quantitative characteristics was not yet explained.

c. The effect of oxygen concentration

In photocatalytic oxidation, oxygen acts as a reactant. Hence, the variations of its concentration in solution should change the oxidation rate. However, photocatalytic experiments as a rule included no measurements of the dissolved oxygen concentration. The dissolved oxygen concentration is proportional to its concentration in the gas passed through the reaction mixture. After replacement of air by oxygen, a slight increase in the decomposition rates of methyl phenyl sulfide and benzimidazol-2-yl methyl sulfide was observed.[122] The oxidation of certain thiols was carried out at varying the oxygen flow rate through 20 ml of a Degussa P25 TiO_2 suspension. It turned out that the substrate consumption rate reached its maximum at a flow rate of 1 ml min^{-1}. The further intensification of the oxygen flow somewhat decreased the reaction rate.[77] This was probably associated with the displacement of the irradiated suspension by oxygen bubbles and the decrease in the light absorption by the photocatalyst, because the reaction mixture volume was very small.

d. The effect of substrate concentration

The rate of a liquid-phase photocatalytic reaction usually increases with the increase in the substrate concentration. In the course of photocatalytic oxidation, numerous intermediates and final products were formed. The oxidation rate (W) of the original substrate on heterogeneous photocatalysts is often described by the following equation:

$$W = \frac{kK_S C_S}{1 + K_S C_S + \sum_i K_i C_i},$$

where subscript S corresponds to the original substrate and i corresponds to various substances formed during the reaction or initially present as a buffer solution; k is the rate constant of the rate-limiting step, K is the adsorption constant and C is the concentration. Usually, K_i and C_i values are unknown and this severely complicates the description of the oxidation kinetics at high degrees of conversion. In the beginning of a reaction, only substrate S and, probably, buffer solution components are present. Hence, the primary oxidation rate is often well described by the following much simpler equation:[99]

$$W = \frac{kK_S C_S}{1 + K_S C_S}. \quad (1)$$

The oxidation rate increases with an increase in the substrate concentration and reaches a plateau at a concentration corresponding to the monolayer coverage of the catalyst surface. Correspondingly, at high original substrate concentrations, the initial segment of kinetic curves was linear. For low initial concentrations, the kinetic curve should be approximated by exponential decay. Actually, the kinetic curves are often described by the exponential decay even for high initial substrate concentrations, which can be explained by the formation of intermediate products that compete with the original substrate.

e. The effect of solvent

Photocatalytic reactions are, in fact, charge transfer reactions. For TiO_2, photogenerated electrons and 'holes' interact with the reactant species located near the TiO_2 surface to form the corresponding reduced or oxidised products. For reduced sulfur compounds, the standard potential of formation of radical cations is usually substantially lower than the potential of formation of hydroxyl radicals from water. This is why the direct oxidation of organosulfur compounds should prevail over the reactions of hydroxyl radical formation. The resulting hydroxyl radicals can also generate the oxidation of reduced sulfur compounds to form radical cations, as was shown for the photocatalytic oxidation of several types of aromatic sulfur compounds.[68, 69]

The effect of solvent polarity on the radical cation solvation energy is roughly described by the Born equation. Therefore, solvents with high dielectic constants (ε) favour the formation of radical cations. A correlation between the photocatalytic oxidation rate and the solvent dielectric constant was found experimentally for reactions of methyl phenyl sulfide and benziminazol-2-yl methyl sulfide on TiO_2.[126] The highest oxidation rate was observed in water ($\varepsilon = 80$) and severely decreased in the following series of solvents: acetonitrile ($\varepsilon = 38$) > methanol ($\varepsilon = 33$) > ethanol ($\varepsilon = 24$) > CCl_4 ($\varepsilon = 2.2$). These data are consistent with the necessity of the radical cation stabilisation by the solvent for a reaction to be efficient.

f. The effect of added oxidants

Hydrogen peroxide can directly react with organic compounds of reduced sulfur in solutions exposed to ultraviolet radiation. The H_2O_2 reaction with sulfides leads to sulfoxides and sulfones. Dibenzothiophene conversion reached 54% in the course of 8-h irradiation when a 3% H_2O_2 solution in acetonitrile was used and the starting dibenzothiophene concentration was 0.5 mmol $litre^{-1}$ (Ref. 74). Photocatalytic oxidation of dibenzothiophene was twice faster in the presence of H_2O_2; however, this result could also be achieved in the direct dibenzophenone oxidation by hydrogen peroxide under the mercury-xenon lamp radiation.[74] Under the same conditions, the direct oxidation rate of 4,6-dimethyldibenzothiophene decreased upon the addition of titanium dioxide. Hence, addition of H_2O_2 is probably inefficient in the liquid-phase photocatalytic oxidation of organic compounds of sulfur in low oxidation states as compared with their photolysis. This situation can be radically different if the ultraviolet radiation with the wavelength > 300 nm is used. Under these conditions, no radiation-induced H_2O_2 decomposition occurs, and the reaction can follow only the photocatalytic or thermal routes.

Addition of persulfates can increase the photocatalytic oxidation rate of sulfur compounds. For the methylparathion oxidation on TiO_2, the oxidation rate increased approximately 1.5-fold with the addition of 0.5 mmol $litre^{-1}$ $K_2S_2O_8$ but remained unchanged with the further increase in the concentration of this oxidant.[99]

3. Kinetic dependences of gas-phase reactions

Under normal conditions, gas-phase reactions of sulfur compounds inevitably lead to the catalyst deactivation. However, the characteristic features of oxidation kinetics can be studied before the onset of deactivation. Titanium dioxide with its highly developed surface was the most active photocatalyst.[41] Modifying TiO_2 with ammonium cations can increase the reaction rate, as was observed for methanethiol.[27] Such an effect was probably associated with

the stronger adsorption of MeSH on NH_4^+/TiO_2. Silver deposition on TiO_2 increased the conversion of H_2S and MeSH, apparently also due to the stronger adsorption of substrates.[22] The effects of key factors on the rate of gas-phase heterogeneous photocatalytic oxidation of sulfur compounds is considered below.

a. The effect of temperature

Elevation of temperature usually accelerates the oxidation of sulfur-containing compounds. For the photocatalytic oxidation of ethanethiol, as the temperature varied from 100 to 180 °C, the reaction rate constant increased from 0.4 to 5.0 mmol m^{-3} s^{-1}, while the Langmuir adsorption constant decreased from 371 to 24 m^3 mol^{-1}. The opposite effects of the rate and adsorption constants led to a slight increase in the ethanethiol conversion as the temperature increased.[28] The observed activation energy was 42 kJ mol^{-1}, while the adsorption entropy was assessed as -70 J mol^{-1} K^{-1} and the adsorption enthalpy was -45 kJ mol^{-1}.

In the photocatalytic oxidation of 2-phenethyl 2-chloroethyl sulfide, as the temperature increased from 40 to 60–70 °C, the initial reaction rate increased, but the time before the onset of photocatalyst deactivation became much shorter.[70] It was reported[48] that quantum yields of 2-chloroethyl ethyl sulfide oxidation decreased as the temperature increased from 20 to 80 °C. Apparently, this was associated with the faster deactivation due to the accumulation of the intermediate and final products at elevated temperatures. As the temperature increased, the amount of adsorbed water dramatically decreased, increasing the photocatalyst sensitivity with respect to accumulation of reaction products. It was assumed that polar reaction products could be accumulated in a polylayer water film that covered the photocatalyst surface.[42]

b. The effect of photocatalyst amount

The rate of gas-phase photocatalytic reactions increased with the increase in the phtotocatalyst weight because the fraction of absorbed light also increased. Upon reaching a photocatalyst amount corresponding to the total opacity for light, the rate reached a plateau.[27] The dependences of the dimethyl disulfide oxidation rate on the titanium dioxide and zinc oxide weights were shown[39] to simultaneously reach plateaus at a photocatalyst weight above 5 mg cm^{-2}. However, it was demonstrated[42] that with further increase in the TiO_2 weight, both the total oxidation rate and the amount of converted disulfide increased before the onset of photocatalyst deactivation. This is because with the increase in the photocatalyst weight, the number of adsorption sites suitable for accommodation of the intermediate and final products of photocatalytic reactions of substrates increases. Apparently, the products were capable of relatively freely moving over the photocatalyst layer.

c. The effect or air humidity

The effect of the moisture content in air was often considered when studying the photocatalytic oxidation of reduced sulfur organic compounds. The photocatalytic reduction of methanethiol occurred at the maximum rate for the relative air humidity of 43%.[27] For the lower and higher moisture contents, the MeSH conversion decreased. Methanethiol is a weak acid ($pK_a = 10.3$). Moderate amounts of adsorbed water apparently dissolve the substrate increasing its surface concentration. Moreover, water can dissolve the reaction products. Sulfinic, sulfonic and sulfuric acids can vacate the reaction sites by being dissolved in polylayers of adsorbed water.

The photocatalytic oxidation of diethyl sulfide (DES) in a reactor with a short time of contact was shown to be optimal at a high relative air humidity (>19%) if the illumination intensity was low (1.1 mW cm^{-2}). And *vice versa*, for UV radiation of relatively high intensity (11 mW cm^{-2}), a low humidity level favoured the consumption of the largest DES amounts during a given period.[40] Such an effect can be partly explained by heating of the photocatalyst surface. However, by and large, this was probably associated with the different rates of generation of reaction products, namely, for the high light intensity, a substantial amount of water was formed, which increased it original concentration.

For dimethyl sulfide oxidation, the highest conversion rate was reached at about 20% relative humidity (at 25 °C).[30] However, when the dimethyl disulfide photocatalytic oxidation was carried out on titanium dioxide in a differential reactor, the deep oxidation rate decreased with the increase in the water vapour concentration.[39] It follows from the shown results that the optimal humidity level depends on other reaction conditions.

d. The effect of substrate concentration

The effect of the oxidisable substance concentration is conventionally described by the Langmuir–Hinshelwood model with adsorption sites of one kind. Adequate agreement between the theory and experimental data is usually achieved, especially, when a narrow range of substrate concentrations is used.[39] To check the correctness of using this model, the linear form of equation (1) is used

$$\frac{1}{W} = \frac{1}{kKC} + \frac{1}{k}.$$

Thus it was shown that the dependence of the diethyl disulfide photocatalytic oxidation rate is well described by this equation and reaches a plateau at a concentration above 100 ppm.[39]

For low oxidisable substrate concentrations, the oxidation rate often corresponds to a first-order reaction. This agrees with the Langmuir–Hinshelwood equation if the surface coverage is far below a monolayer, *i.e.*, $KC \ll 1$. A linear dependence of the oxidation rate on the concentration was observed for H_2S.[17]

When the reaction was carried out in a static system, the kinetic plot of the dimetyl sulfide concentration was well described by the first-order reaction equation. In this case, the rate constant of a first-order reaction decreased with the increase in the initial dimethyl sulfide concentration.[33] Such a behaviour was associated with the rapid development of photocatalyst deactivation with the increase in the substrate concentration. Oxidation of an adsorbed CEES monolayer was well described by the first-order kinetics as regards both the initial substance and the oxidation products accumulated on the surface; moreover, the characteristic times of these processes were different.[44]

e. The effect of added oxidants

Addition of hydrogen peroxide in the gas-phase photocatalytic oxidation could have both positive and negative effects on the reaction rate.[127] The opposite effects were associated with the different reaction rates between a sub-

strate and hydrogen peroxide. For example, acetone quickly reacted with H_2O_2 vapours, whereas benzene did not virtually react with them in the absence of catalysts. Organic sulfur compounds are known to undergo oxidation in the presence of hydrogen peroxide. Apparently, it is for this reason that the addition of H_2O_2 vapour to the original diethyl sulfide oxidation mixture increased the reaction rate by 10%–20%.[41] The small effect was probably due to a small concentration of H_2O_2 that managed to reach the reactor. In further studies, saturated H_2O_2 vapours should be used which may allow one to carry out photocatalytic oxidation at a substantially high rate and delay the photocatalyst deactivation.

4. The role of photochemical reactions

Organic compounds of reduced sulfur undergo photochemical oxidation even in the absence of sensitisers or photocatalysts. Absorption of a quantum of UV radiation by sulfides or disulfides resulted in the cleavage of C–S or S–S bonds.[128]

$$R_2S \xrightarrow{h\nu,\ \lambda < 300\ nm} R^{\bullet} + RS^{\bullet},$$

$$R_2S_2 \xrightarrow{h\nu,\ \lambda < 300\ nm} 2\,RS^{\bullet}.$$

The formed thiyl radicals $RS^{\bullet}$ reacted with molecular oxygen to form thiylperoxide radicals $RSO_2^{\bullet}$ later transformed to various photolysis products. The main sulfur-containing products of the photolysis of sulfides and disulfides are as follows:[128]

$$RS^{\bullet} \xrightarrow{O_2} RSO_3H + RSO_2H + RS(O)_2SR + H_2SO_4 + SO_2.$$

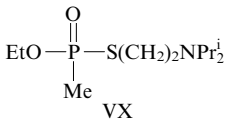
It deserves mentioning that the sulfide and disulfide products in purely photochemical reactions resemble very much their products in photocatalytic oxidation. This means similar reaction mechanisms.

Photocatalytic reactions are often carried out under the mercury-lamp light. Low-pressure mercury lamps mainly emit light with the wavelength of 253.7 nm while the radiation of mercury lamps of moderate and high pressure has maxima at 254, 365 nm, *etc*. The photocatalysis on TiO_2 requires radiation with the wavelength below 400 nm, whereas the direct photolysis can occur under the radiation with the wavelength of 254 nm. Emission of moderate-pressure mercury lamps is the most intense in the vicinity of 365 nm. This is why, for photocatalysis and photolysis with equal quantum yields, the photocatalytic reaction rate should be higher when a moderate-pressure lamp is used. However, the quantum yield of direct photolysis is apparently substantially higher as compared with photocatalytic oxidation.

Particularly, it was found that PECES undergoes both photolysis and photocatalytic oxidation when a TiO_2 suspension is irradiated by a moderate-pressure mercury lamp. Dissolution of this compound led to its hydrolysis. Under UV radiation, both PECES as such and its hydrolysis products (HEPES) were transformed into inorganic products. The simultaneous photolysis and photocatalysis under the overall radiation of a moderate-pressure mercury lamp led to complete mineralisation in 250 min. If light with $\lambda < 300$ nm was filtered out by a pyrex filter, the complete oxidation took more than 600 min. No photolysis occurred under such radiation.[70] Thus, under the moderate-pressure mercury lamp radiation, the photolysis can be much more efficient as compared with the photocatalytic oxidation.

It was proposed to use photolysis as a decontamination method. Irradiation of yperite vapours and droplets led to its chemical transformations. Under illumination at a wavelength of 254 nm, the gas-phase photolysis proceeded faster than photocatalytic oxidation[54] and produced nonvolatile products of the presumably polymeric nature, which were deposited on the reactor walls and a quartz window that let radiation in. The main identified products were bis(2-chloroethyl) disulfide and bis(2-chloroethyl) sulfoxide. A polymer that contained $-SCH_2CH_2Cl$ and $-OCH_2CH_2Cl$ groups was also among the main reaction products.[129] The high toxicity of yperite was caused by the presence of $-SCH_2CH_2Cl$ groups that can alkylate skin proteins, causing blisters. Insofar as these groups are not removed by the photolysis, the latter cannot be considered as an efficient decontamination method. The disulfide formation as the main reaction product suggests that the cleavage of the carbon–sulfur bond is the main photolysis channel.

Another CWA, VX, was subjected to photolysis in the liquid phase. This compound actively absorbs radiation with the wavelength of 230 nm. Illumination with a bactericidal lamp led to various products in the liquid and gas phases.[130] The main identified products were diisopropylaminoethanethiol, thioethyl ethyl methylphosphonate and other compounds containing the phosphorus–sulfur bond. The composition of formed products points to the cleavage of several bonds during the primary photochemical reactions, namely, P–S, S–C and C–N. Isomerisation reactions proceeded with participation of both the original VX agent and the products of its photochemical reactions.



VX

Decomposition of gas-phase organic sulfur compounds in air, induced by the light of a mercury bactericidal lamp, probably involved ozone formed under the UV irradiation. Methanethiol was removed rather efficiently from air when illuminated at a wavelength of 253.7 nm, whereas irradiation at 365 nm did not induce this reaction.[27] Methanethiol has two absorption bands (at 230 and 205 nm) located relatively far from the emission band of a low-pressure mercury lamp. Hence, the contribution of methanethiol reactions with ozone to the photolysis process cannot be ruled out.

In contrast to sulfides and disulfides, the photolysis of pesticides (for example, insecticide fenitrothion) proceeded substantially more slowly than the photocatalytic oxidation and led to the formation of other intermediate products.[90] Apparently, this was caused by the fact that the benzene ring is the chromophore of fenitrothion, but, in the photocatalytic oxidation, the attack of hydroxyl radicals is preferentially directed to the sulfur atom.

V. Deactivation and reactivation of catalysts

1. Liquid-phase reactions

Reactions of liquid-phase photocatalytic oxidation often demonstrate no photocatalyst deactivation. Reaction products could be efficiently removed from the photocatalyst

surface to solution. However, in certain cases, photocatalytic oxidation resulted in photocatalyst deactivation. Products of these reactions were insoluble in the solvents used. One of examples represents the destruction of a pesticide, vapam, in an aqueous TiO_2 suspension. The sulfur deposition on the catalyst surface was revealed by photoelectron spectroscopy after the photocatalyst destruction. Changes in the photocatalyst surface were responsible for the gradual decay in the catalytic activity in five successive runs of vapam destruction.[111]

Yet another example is the compound PECES, a CWA simulant. For the decomposition of this substance in an aqueous TiO_2 suspension, it was found that numerous products were accumulated on the photocatalyst surface, among which 2-phenethyl sulfide (75%) and 2-phenethyl sulfinic acid (10%) prevailed.[70] Comparison of the photocatalytic activity in the PECES and dimethyl methylphosphonate (DMMP) oxidation has shown that the oxidation rate of the latter is substantially higher. This can be explained by the fact that the DMMP oxidation produced no insoluble products capable of occupying the reaction sites on the catalyst surface.

2. Gas-phase reactions

Photocatalyst deactivation is often observed in gas-phase reactions of photocatalytic oxidation of sulfur compounds on solid photocatalysts. Sulfuric acid is the final oxidation product of a sulfur compound on titanium dioxide. Being non-volatile at room temperature, it is accumulated on the photocatalyst surface and blocks its active sites. Accumulation of intermediate oxidation products could also be responsible for the catalyst deactivation.

The onset of catalyst deactivation manifests itself by a decrease in the CO_2 formation rate. Intermediate oxidation products appears in the gas phase in large concentrations. After the complete catalyst deactivation, the substrate conversion is totally absent. Photocatalyst deactivation was observed experimentally in the oxidation of hydrogen sulfide,[17] dimethyl sulfide (DMS),[30,31] dimethyl disulfide,[37,39] diethyl sulfide,[40,42,43] CEES[49,51] and PECES.[70]

Deactivation of the TiO_2 surface during the DES decomposition was studied relatively thoroughly as a function of the reaction conditions. It was shown that the accessible catalyst surface is the key factor that determines the DES amount converted before the onset of deactivation. The increase in the TiO_2 surface in a sequence 50, 75, 120 and 340 $m^2\,g^{-1}$ led to an increase in the amount of consumed substrate at a constant catalyst weight in the reactor. Analogously, with the increase in the TiO_2 catalyst weight in the reactor from 180 to 330 mg, the DES weight converted prior to deactivation increased from 5 to 6.5 $\mu mol\,m^{-2}$.

Water vapours had a substantial effect on the DMS and DES photocatalytic oxidation, and the mechanism of this effect depended on the reaction conditions. Water molecules usually displace other molecules from the photocatalyst surface. When large amounts of adsorbed substances were present on the surface, water could assist the oxidation by partially vacating the sites for oxygen adsorption. Water polylayers can dissolve the substances located on the surface. On the other hand, if the number of oxidisable molecules on the surface was small, then water would decrease the oxidation rate due to the needless removal of adsorbed molecules. This was observed in the DES oxidation. Before the catalyst deactivation developed, increasing water vapour concentration from 1900 to 22 000 ppm had a profoundly negative effect on the oxidation rate. After the beginning of catalyst deactivation, the complete substrate oxidation to inorganic products virtually stopped. Moreover, an increase in the water vapour concentration increased the DES conversion. Very dry air always had a negative effect on the oxidation rate, because water plays an important role in the separation of photogenerated charges on the TiO_2 surface.

The DES concentration in the reaction inlet also affected its conversion reached before the onset of deactivation. The amount of converted DES increased from 6.5 to 13.7 $\mu mol\,m^{-2}$, if the substrate concentration in the initial reaction mixture decreased from 350 to 87 ppm (Ref. 42). This was due to the fact that at low diethyl sulfide concentrations, the reaction was closer to an equilibrium process. The complete oxidation product, sulfuric acid, had more time to diffuse to non-illuminated photocatalyst parts. The incomplete oxidation products were formed in smaller amounts at a low DES concentration, leaving a larger number of reaction sites for sulfuric acid.

At high DES concentrations, the complete oxidation process was hindered, and partial oxidation prevailed. Such behaviour was usually observed in a static gas reactor. The photocatalytic DES oxidation demonstrated an induction period in the carbon dioxide evolution.[43] During this period, the rate of CO_2 evolution was very low. After the DES consumption from the gas phase was virtually completed, the induction period came to end and fast CO_2 evolution began. After the successive oxidation of several DES portions on the same catalyst, the catalyst was deactivated. Moreover, in each subsequent run, the induction period became longer. To explain this phenomenon, it should be borne in mind that DES and diethyl disulfide (DEDS) have the lower ionisation potentials (8.4 eV) than any other intermediate product of DES oxidation. This is why the photogenerated 'holes' preferentially react with DES and DEDS rather than with other substances on the TiO_2 surface. Correspondingly, the oxidation of the other intermediates can start only after DES and DEDS on the surface have been consumed.

Deactivated catalysts can usually be regenerated by one or another procedure. The following procedures of catalyst reactivation were tried.

1. Long-term UV radiation of deactivated photocatalyst in moist air.[42] This procedure makes it possible to achieve only partial reactivation of the catalyst, namely, the DES conversion was merely 1.6 $\mu mol\,m^{-2}$ compared with 5 $\mu mol\,m^{-2}$ before deactivation.

2. UV irradiation of a deactivated photocatalyst in moist air up to the cessation of CO_2 evolution, followed by rinsing with water. This method allows one to achieve almost complete reactivation, *viz*., the DES conversion on a reactivated catalyst was 4 $\mu mol\,m^{-2}$. A disadvantage of this procedure is its long duration. At the same time, rinsing water contained only sulfuric acid.[42]

3. Rinsing with water. This fast procedure allows virtually complete reactivation; thus the DES conversion was 3.9 $\mu mol\,m^{-2}$ on the reactivated catalyst. However, water used for rinsing contained considerable amounts of partial oxidation products and sulfuric acid. This rinsing water required further treatment.[42]

4. Thermal treatment. Heating[51] of a deactivated catalyst at 124 °C led to the recovery of approximately a third of its original activity. This treatment is equivalent to the first

of listed procedures. Indeed, the thermal treatment removes all partial oxidation products from the surface; only H_2SO_4 and sulfonic acids are left.

Rinsing with water made it possible to completely recover the catalyst activity. However, a part of initial activity was permanently lost. It is well known that concentrated sulfuric acid dissolves TiO_2. There is good reason to assume that H_2SO_4 etches the TiO_2 surface during long-term sulfide oxidation. According to the IR spectroscopic data, bidentate sulfates are present on the TiO_2 surface after its reactivation by rinsing with water.[49] This suggests that irreversible changes in TiO_2 are developed as it is deactivated during the oxidation of sulfur compounds.

VI. Conclusion

Studying photocatalytic and photolytic transformations of reduced sulfur compounds has demonstrated the wide diversity of reaction routes of these compounds. Photocatalytic methods allow one to carry out both the oxidation and evolution of hydrogen, the reduction and the synthesis. In the hydrogen oxidation and evolution, the low ionisation and redox potentials make the electron transfer from molecules of reduced sulfur compounds the most advantageous process leading to the formation of radical cations. Further reactions lead to the cleavage of the carbon–sulfur or sulfur–sulfur bonds for (poly)sulfides and also to the oxidation of sulfur atoms to form sulfoxides, sulfones, thiosulfonates. In reactions of aromatic molecules, the radical centre can be located far from the sulfur atom so that the reactions will include the oxidation of side groups or other radical reactions including polymerisation. When a molecule contains other heteroatoms, for example, nitrogen, then heterocycles can be formed apparently as a result of radical reactions. The intermediate oxidation products undergo further reactions to ultimately yield inorganic products.

Reactions of gas-phase photocatalytic oxidation proceed with considerably higher quantum yields as compared with liquid-phase reactions. Gas-phase photocatalytic reactions of sulfur compounds are accompanied by the catalyst deactivation due to accumulation of oxidation products on its surface. Liquid-phase oxidation can be accompanied by deactivation if the products are insufficiently soluble in the solvent or strongly bound to the catalyst surface. Efficient ways of catalyst reactivation consist of washing the oxidation products off from the surface. The surface area is the decisive factor that determines the amounts of substances capable of reacting before the deactivation.

In liquid phase, the oxidation processes are very sensitive to the solution composition, the latter determining how readily the reaction of an oxidisable substance with a photocatalyst will proceed.

The high efficiency of gas-phase photocatalytic oxidation of organosulfur substances make it possible to propose this method for cleaning air, particularly, from highly toxic compounds.

The prospects for using photocatalytic oxidation for water cleaning were experimentally confirmed by Spanish scientists who used large (250 litre) solar photocatalytic reactors with parabolic reflectors in the decomposition of dissolved pesticides.[107, 115]

The author is grateful to the leaders of the Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences and scientists of the group dealing with photocatalysis on semiconductors for their priceless assistance in carrying out experimental and theoretical studies included in this review.

This review was prepared with the partial financial support of NATO (Project SfP-981461) and the International Science and Technology Center (Project No. 3305).

References

1. V N Parmon, in *Fotokataliticheskoe Preobrazovanie Solnechnoi Energii: Geterogennye, Gomogennye i Molekulyarnye Strukturno-organizovannye Sistemy* (Photocatalytic Conversion of Solar Energy: Heterogeneous, Homogeneous and Molecular Structurally Organised Systems) (Novosibirsk: Nauka, 1991) p. 7
2. S E Braslavsky *Pure Appl. Chem.* **79** 293 (2007)
3. N J Turro *Modern Molecular Photochemistry* (Sausalito, CA: University Science Books, 1991)
4. A B Callear *Chem. Rev.* **87** 335 (1987)
5. L A Fowley, J C Lee, R H Crabtree, P E M Siegbahn *Organometallics* **15** 1157 (1996)
6. A Mills, S Le Hunte *J. Photochem. Photobiol., A* **108** 1 (1997)
7. M A Fox, M T Dulay *Chem. Rev.* **93** 341 (1993)
8. O Carp, C L Huisman, A Reller *Prog. Solid State Chem.* **32** 33 (2004)
9. T L Thompson, J T Yates *Chem. Rev.* **106** 4428 (2006)
10. R S Glass, University Science Books in *Sulfur Radical Cations (Topics in Current Chemistry)* (Berlin: Springer, 1999) Vol. 205, p. 1
11. G V Buxton, C L Greenstock, W P Helman, A B Ross *J. Phys. Chem. Ref. Data* **17** 513 (1988)
12. B Mills *Filtration Separation* **2** 147 (1995)
13. F W Mc Lafferty, F Turecek *Interpretation of Mass Spectra* (Sausalito, CA: University Science Books, 1993)
14. P Wardman *J. Phys. Chem. Ref. Data* **18** 1637 (1989)
15. H Yokoi, A Hatta, K Ishiguro, Y Sawaki *J. Am. Chem. Soc.* **120** 12728 (1998)
16. T Tachikawa, S Tojo, M Fujisuka, T Majima *Langmuir* **20** 4327 (2004)
17. M R Canela, R M Alberici, W F Jardim *J. Photochem. Photobiol., A* **112** 73 (1998)
18. T Kato, A Nakajima, T Watanabe, K Hashimoto *Res. Chem. Intermed.* **31** 371 (2005)
19. S Kataoka, E Lee, M I Tejedor-Tejedor, M A Anderson *Appl. Catal. B* **61** 159 (2005)
20. R Portela, B Sanchez, J M Coronado *J. Adv. Oxid. Tech.* **10** 375 (2007)
21. R Portela, B Sanchez, J M Coronado, R Candal, S Suarez *Catal. Today* **129** 223 (207)
22. S Kato, Y Hirano, M Iwata, T Sano, K Takeuchi, S Matsuzawa *Appl. Catal. B* **57** 109 (2005)
23. J S Jang, W Li, S H Oh, J S Lee *Chem. Phys. Lett.* **425** 278 (2006)
24. J S Jang, H G Kim, P H Borse, J S Lee *Int. J. Hydrogen Energy* **32** 4786 (2007)
25. K Schoumacher, C Geantet, M Lacroix, E Puzenat, C Guillard, J M Herrmann *J. Photochem. Photobiol., A* **152** 147 (2002)
26. K Suzuki, S Satoh, T Yoshida *Denki Kagaku* **59** 521 (1991)
27. X Z Li, M F Hou, F B Li, H Chua *Ind. Eng. Chem. Res.* **45** 487 (2006)
28. A Kachina, S Preis, J Kallas *Environ. Chem. Lett.* **4** 107 (2006)
29. J Peral, D F Ollis *J. Mol. Catal. A* **115** 347 (1997)
30. K Demeestere, J Dewulf, B D Witte, H V Langenhove *Appl. Catal. B* **60** 93 (2005)
31. N González-Garcia, J A Ayllón, X Doménech, J Peral *Appl. Catal. B* **52** 69 (2004)
32. T Tanizaki, Y Murakami, Y Hanada, S Ishikawa, M Suzuki, R Shinohara *J. Health Sci.* **53** 514 (2007)
33. K Demeestere, J Dewulf, T Ohno, P H Salgado, H V Langenhove *Appl. Catal. B* **61** 140 (2005)
34. V Latour, T Pigot, P Mocho, S Blanc, S Lacombe *Catal. Today* **101** 359 (2005)

35. C Cantau, T Pigot, R Brown, P Mocho, M T Maurette, F Benoit-Marque, S Lacombe *Appl. Catal. B* **65** 77 (2006)
36. C Cantau, S Larribau, T Pigot, M Simon, M T Maurette, S Lacombe *Catal. Today* **122** 27 (2007)
37. H.Nishikawa Y.Takahara. *J. Mol. Catal. A* **172** 247 (2001)
38. M C Canela, R M Alberici, R C R Sofia, M N Eberlin, W F Jardim *Environ. Sci. Technol.* **33** 2788 (1999)
39. C Guillard, D Baldassare, C Duchamp, M N Ghazzal, S Daniele *Catal. Today* **122** 160 (2007)
40. A V Vorontsov, D V Kozlov, P G Smirniotis, V N Parmon *Kinet. Katal.* **46** 450 (2005) [a]
41. A V Vorontsov, E N Savinov, L Davydov, P G Smirniotis *Appl. Catal. B* **32** 11 (2001)
42. A V Vorontsov, E N Savinov, C Lion, P G Smirniotis *Appl. Catal. B* **44** 25 (2003)
43. D V Kozlov, A V Vorontsov, P G Smirniotis, E N Savinov *Appl. Catal. B* **42** 77 (2003)
44. D A Panayotov, D K Paul, J T Yates *J. Phys. Chem. B* **107** 10571 (2003)
45. S M Bonesi, M Freccero, A Albini *J. Phys. Org. Chem.* **12** 703 (1999)
46. J Eriksen, C S Foote, T L Parker *J. Am. Chem. Soc.* **99** 6455 (1977)
47. M A Fox, Y-S Kim, A A Abdel-Wahab *Catal. Lett.* **5** 369 (1990)
48. I N Martyanov, K J Klabunde *Environ. Sci. Technol.* **37** 3448 (2003)
49. A V Vorontsov, C Lion, E N Savinov, P G Smirniotis *J. Catal.* **220** 414 (2003)
50. T L Thompson, D A Panayotov, J T Yates, I Martyanov, K Klabunde *J. Phys. Chem. B* **108** 17857 (2004)
51. D Panayotov, P Kondratyuk, J T Yates *Langmuir* **20** 3674 (2004)
52. S T Han, G Y Zhang, H L Xi, D N Xu, X Z Fu, X X Wang *Catal. Lett.* **122** 106 (2008)
53. Y-C Yang, in *Photocatalytic Oxidation of Mustard Using Semiconductor Oxides* (CRDEC, 1989) p. 83
54. G-M Zuo, Z-X Cheng, G-W Li, W-P Shi, T Miao *Chem. Eng. J.* **128** 135 (2007)
55. N Soggiu, H Cardy, J L H Jivan, I Leray, J P Soumillion, S Lacombe *J. Photochem. Photobiol., A* **124** 1 (1999)
56. R S Davidson, J E Pratt *Tetrahedron Lett.* **52** 5903 (1983)
57. S Lacombe, H Cardy, M Simon, A Khoukh, J P Soumillion, M Ayadim *Photochem. Photobiol. Sci.* **1** 347 (2002)
58. E Baciocchi, T D Giacco, F Elisei, M F Gerini, M Guerra, A Lapi, P Liberali *J. Am. Chem. Soc.* **125** 16444 (2003)
59. A V Vorontsov, L Davydov, E P Reddy, C Lion, E N Savinov, P G Smirniotis *New J. Chem.* **26** 732 (2002)
60. A V Vorontsov, Y-C Chen, P G Smirniotis *J. Hazard. Mater. B* **113** 89 (2004)
61. E Baciocchi, T D Giacco, M I Ferrero, C Rol, G V Sebastiani *J. Org. Chem.* **62** 4015 (1997)
62. H Vosooghian, M H Habibi *Int. J. Photoenergy* 89759 (2007)
63. M A Fox, A A Abdel-Wahab *Tetrahedron Lett.* **31** 4533 (1990)
64. E Baciocchi, C Crescenzi, O Lanzalunga *Tetrahedron* **53** 4469 (1997)
65. W Adam, J E Arguello, A B Penenory *J. Org. Chem.* **63** 3905 (1998)
66. E Baciocchi, T D Giacco, F Elisei, A Lapi *J. Org. Chem.* **71** 853 (2006)
67. N Somasundaram, C Srinivasan *J. Photochem. Photobiol., A* **115** 169 (1998)
68. T Tachikawa, S Tojo, M Fujitsuka, T Majima *Chem. Phys. Lett.* **382** 618 (2003)
69. T Tachikawa, S Tojo, M Fujitsuka, T Majima *Chem.–Eur. J.* **12** 7585 (2006)
70. A V Vorontsov, A A Panchenko, E N Savinov, C Lion, P G Smirniotis *Environ. Sci. Technol.* **36** 5261 (2002)
71. M Sokmen, D W Allen, A T Hewson, M R Clench *J. Photochem. Photobiol., A* **141** 63 (2001)
72. M Alvaro, E Carbonell, M Espla, H Garcia *Appl. Catal. B* **57** 37 (2005)
73. A A Abdel-Wahab, A E M Gaber *J. Photochem. Photobiol., A* **114** 213 (1998)
74. S Matsuzawa, J Tanaka, S Sato, T Ibusuki *J. Photochem. Photobiol., A* **149** 183 (2002)
75. H Mei, B W Mei, T F Yen *Fuel* **82** 405 (2003)
76. J Robertson, T J Bandosz *J. Colloid Interface Sci.* **299** 125 (2006)
77. M H Habibi, S Tangestaninejad, B Yadollahi *Appl. Catal. B* **33** 57 (2001)
78. F B Li, X Z Li, M F Hou *Appl. Catal. B* **48** 185 (2004)
79. A V Vorontsov, C Charvy, C Lion *Top. Catal.* **35** 245 (2005)
80. H Tada, K Teranishi, Y Inubushi, S Ito *Langmuir* **16** 3304 (2000)
81. C Dominguez, J Garcia, M A Pedraz, A Torres, M A Galan *Catal. Today* **40** 85 (1998)
82. P L Huston, J J Pignatello *Water Res.* **33** 1238 (1999)
83. I Oller, W Gernjak, M I Maldonado, P Fernandez-Ibanez, J Blanco, J A Sánchez-Pérez, S Malato *Environ. Chem. Lett.* **3** 118 (2005)
84. E Evgenidou, I Konstantinou, K Fytianos, T Albanis *J. Hazard. Mater. B* **137** 1056 (2006)
85. I Oller, S Malato, J A Sánchez-Pérez, M I Maldonado, R Gasso *Catal. Today* **129** 69 (2007)
86. I Oller, W Gernjak, M I Maldonado, L A Pérez-Estrada, J A Sánchez-Pérez, S Malato *J. Hazard. Mater.* **138** 507 (2006)
87. A Arques, A M Amat, A Garcia-Ripoll, R Vicente *J. Hazard. Mater.* **146** 447 (2007)
88. M Kerzhentsev, C Guillard, J M Herrmann, P Pichat *Catal. Today* **27** 215 (1996)
89. A Topalov, D Molnar-Gabor, B Abramovic, S Korom, D Pericin *J. Photochem. Photobiol., A* **160** 195 (2003)
90. P Kormali, D Dimoticali, D Tsipi, A Hiskia, E Papaconstantinou *Appl. Catal. B* **48** 175 (2004)
91. P Kormali, A Troupis, T Triantis, A Hiskia, E Papaconstantinou *Catal. Today* **124** 149 (2007)
92. Z Mengyue, C Shifu, T Yaowu *J. Chem. Technol. Biotechnol.* **64** 339 (1995)
93. S F Chen, M Y Zhao, Y W Tao *Microchem. J.* **54** 54 (1996)
94. R Doong, W Chang *J. Photochem. Photobiol., A* **116** 221 (1998)
95. V A Sakkas, D A Lambropoulou, T M Sakellarides, T A Albanis *Anal. Chim. Acta* **467** 233 (2002)
96. T-S Kim, J-K Kim, K Choi, M K Stenstrom, K-D Zoh *Chemosphere* **62** 926 (2006)
97. M Nowakowska, M Sterzel, S Zapotoczny, E Kot *Appl. Catal. B* **57** 1 (2005)
98. E Moctezuma, E Leyva, G Palestino, H de Lasa *J. Photochem. Photobiol., A* **186** 71 (2007)
99. E Evgenidou, I Konstantinou, K Fytianos, I Poulios, T Albanis *Catal. Today* **124** 156 (2007)
100. L Li, Q Wu, Y Guo, C Hu *Microporous Mesoporous Mater.* **87** 1 (2005)
101. X D Yu, Q Y Wu, S C Jiang, Y H Guo *Mater. Charact.* **57** 333 (2006)
102. S Rengaraj, X Z Li, P A Tanner, Z F Pan, G K H Pang *J. Mol. Catal. A* **247** 36 (2006)
103. A Sanjuan, G Aguirre, M Alvaro, H Garcia *Water Res.* **34** 320 (2000)
104. M B Kralj, M Franko, P Trebse *Chemosphere* **67** 99 (2007)
105. M B Kralj, U Cernigoj, M Franko, P Trebse *Water Res.* **41** 4504 (2007)
106. M Muneer, M Saquib, M Qamar, D Bahnemann *Res. Chem. Int.* **30** 663 (2004)
107. S Malato, J Blanco, C Richter, M I Maldonado *Appl. Catal. B* **25** 31 (2000)
108. E Kozlova, A Vorontsov, G Rima, C Lion, S Preis *Water Sci. Technol.* **55** 133 (2007)
109. R A Doong, W H Chang *J. Photochem. Photobiol., A* **107** 239 (1997)
110. A Garcia-Ripoll, A M Amat, A Arques, R Vicente, M F Lopez, I Oller, M I Maldonado, W Gernjak *Chemosphere* **68** 293 (2007)
111. A Vidal, M A M Luengo *Appl. Catal. B* **32** 1 (2001)
112. I K Konstantinou, T M Sakellarides, V A Sakkas, T A Albanis *Environ. Sci. Technol.* **35** 398 (2001)

113. M Tamimi, S Qourzal, A Assabbane, J-M Chovelon, C Ferronato, Y Ait-Ichou *Photochem. Photobiol. Sci.* **5** 477 (2006)
114. S Malato, J Blanco, A Vidal, D Alarcon, M I Maldonado, J Caceres, W Gernjak *Sol. Energy* **75** 329 (2003)
115. S Malato, J Blanco, C Richter, P Fernandez, M I Maldonado *Sol. Energy Mater. Solar Cells* **64** 1 (2000)
116. I Texier, C Giannotti, S Malato, C Richter, J Delaire *Catal. Today* **54** 297 (1999)
117. I K Konstantinou, V A Sakkas, T A Albanis *Appl. Catal. B* **34** 227 (2001)
118. N Somasundaram, C Srinivasan *J. Photochem. Photobiol., A* **99** 67 (1996)
119. O Borio, B M Gawlik, I R Bellobono, H Muntau *Chemosphere* **37** 975 (1998)
120. M Montalti, A Credi, L Prodi, M T Gandolfi *Handbook of Photochemistry* (New York: CRC, Taylor and Francis, 2006)
121. L Palmisano, A Sclafani, in *Heterogeneous Photocatalysis* (Ed. M Schiavello) (New York: Wiley, 1997)
122. T Tachikawa, S Tojo, K Kawai, M Endo, M Fujitsuka, T Ohno, K Nishijima, Z Miyamoto, T Majima *J. Phys. Chem. B* **108** 19299 (2004)
123. E Baciocchi, T D Giacco, O Lanzalunga, A Lapi *J. Org. Chem.* **72** 9582 (2007)
124. M Vogtherr, M Goez *J. Inf. Rec.* **24** 23 (1998)
125. Z Li, A G Kutateladze *J. Org. Chem.* **68** 8236 (2003)
126. M H Habibi, H Vosooghian *J. Photochem. Photobiol., A* **174** 45 (2005)
127. A V Vorontsov *Catal. Commun.* **8** 2100 (2007)
128. E Robert-Banchereau, S Lacombe, J Ollivier *Tetrahedron* **53** 2087 (1997)
129. G M Zuo, Z X Cheng, G W Li, L Y Wang, T Miao *Environ. Sci. Technol.* **39** 8742 (2005)
130. G M Zuo, Z X Cheng, G W Li, L Y Wang, H Chen *J. Phys. Chem. A* **109** 6912 (2005)

[a] — *Kinet. Catal. (Engl. Transl.)*