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AIR POLLUTION: INVOLVEMENT OF OXYGEN RADICALS (A MINI REVIEW)

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In the past decades air pollution has increased worldwide. We also gained more insight into the complex interactions between different air pollutants in the atmosphere as well as their effects on living cells and organisms. It also has been unequivocally shown by several groups in different countries that oxy radicals play an outstanding role in the interconversion of air pollutants as well as during the manifestation of toxic effects. Not only living systems are affected by air pollutants, but also inorganic systems such as buildings and sculptures. In the following overview the most important reactions occuring in the atmosphere as well as effects of oxidative gaseous compounds and particles such as diesel soot and asbestos will be discussed.

KEY WORDS: Air pollution, oxyradicals, photooxidants, toxic oxygen species.

INTRODUCTION

The participation of oxidants during the formation of acid rain as well as in chlorophyll bleaching as one symptom of plants exposed to air pollutants or to other stresses has been known since almost 100 years. In the periodical "Die Gartenlaube" (No. 48, p. 795), Dr. Gustav Holle reported in 1892 that the damage observed in pine trees in the city of Munich was probably due to the formation of sulfuric acid, which has been shown to accumulate continuously in the snow in Munich city gardens. He proposes that sulfuric acid stems from SO_2 released from coal heating, which is oxidized by hydrogenperoxide, also found in the atmosphere, in rain and in snow. Measurements in this direction had been made in the garden of the famous Pettenkofer Institute by the chemist Dr. Sendner and published in 1887 in "*Bayerisches Industrie- und Gewerbeblatt*". Another important step was the publication by Albert F. Woods on the destruction of chlorophyll by oxidizing enzymes in 1899. In "*Zentralblatt für Bakteriologie, Parasitenkunde und Infektions-krankheiten*" Woods published a seminar read before the American association for the advancement of sciences, Columbus, Ohio, August 1899. He describes experiments where leaves are treated with alcoholic solutions and chlorophyll bleaching in light and in dark was observed afterwards. He concludes that chlorphyll bleaching is an oxidative reaction, catalyzed by oxidases and peroxidases, strongly stimulated by light and especially enhanced after partial decompartmentalization of the green tissue. Nowadays we know a little bit more about the basic reactions occuring in the atmosphere or in the plant cell during pigment degradation. The basic principles observed at the end of the last century are still valid, however. In the last decade a vast amount of information has accumulated concerning basic and applied research, sincerely stimulated by the observations on forest decline ("*Waldsterben*") and the corresponding political pressure finally responsible for the increasing financial support of certain scientific projects.

TABLE I
Yearly global emission rates of important air pollutants (after ref.[1])

compound	emission rate (in 10^9 kg/year)			main sources
CO_2	830.000	na)	800.000	respiration, combustion,
		a)	30.000	biol. degredation
CO	3.400	na)	—	mainly combustion
		a)	3.400	
hydrocarbons	1.000	na)	800	trees, motor vehicles,
(without CH_4)		a)	200	industry
CH_4	500	na)	300	swamps, rice fields,
		a)	200	ruminants
SO_2	400	na)	20	coal and oil combustion,
		a)	380	vulcanoes
NO_x	260	na)	10	combustion, flashes
		a)	150	

na) non-anthropogenic
a) anthropogenic

RESULTS AND DISCUSSION

Air pollutants are emitted by natural and anthropogenic sources. The yearly global emissions of CO_2, CO, hydrocarbons, methane, SO_2 NO_x are summarized in Table I. One can clearly deduce from Table I, that especially SO_2 and NO_x are produced by man-made activities whereas for example hydrocarbons and CO_2 are produced mainly by natural activities.[1]

Since we know that especially NO_x, hydrocarbons and SO_2 are interconverted in the atmosphere by several hundreds of single reactions,[2] which are interconnected in an extremely complicated way, SO_2 and NO_x emissions have been carefully followed since a couple of decades. As shown in Figure 1 both, SO_2 and NO_x emissions increase since the middle of the last century (with depressions, indicating the two world wars). In the last years SO_2 emissions seem to decrease in the western countries due to binding onto calcium oxide after the burning process in the power-plants. NO_x, on the other hand, mainly emitted from power-plants and from automobiles, is still increasing. Since the formation of acid rain and photooxidants, such as organic peroxides or ozon are dependent on the basic emission products SO_2, NO_x and hydrocarbons, all following atmospheric reactions are principally dependent on these products.

ATMOSPHERIC CONVERSIONS

Simulated photoreactions in the atmorphere are mainly started by the reaction between NO and oxygen, where ozone is a product and peroxiacetyl-nitrate (PAN) is produced in the presence of certain hydrocarbon precursors such as propene. During illumination propene and NO decrease and NO_2 seems to be produced intermittantly. A continuous increase in aldehydes and ozone after a certain time of

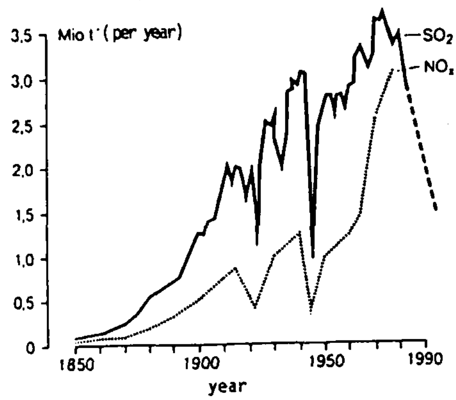


FIGURE 1 SO_2^- and NO_x^- emissions since 1850[1] (W-Germany).

illumination is observed as well as formation of peroxiacetylnitrate (Figure 2). It also has been shown that ozone accumulation occurs time- and light- dependent reaching maxima in the late afternoon. The most important reactions concerning these aspects have been summarized recently by Oßwald and Elstner (1986).[3]

FUNDAMENTAL REACTIVITIES OF MAIN AIR POLLUTANTS

SO_2

SO_2 as the anhydride of hyposulfuric acid is chemically a reductant. In biological systems, however, one-electron donation yields the autooxidizable $HSO_3^{\cdot}$ radical, which undergoes chain reactions with peroxides. This has been documented by the chlorophyll degradation, which is rapidly brought about only in the presence of both a hydroperoxide (LOOH) and sulfite (HSO_3^-) (Figure 3).[4]

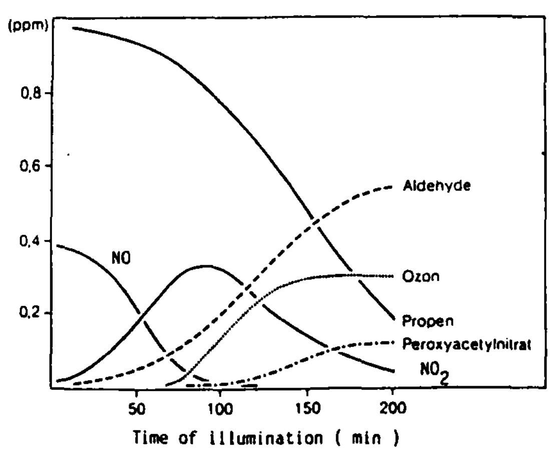
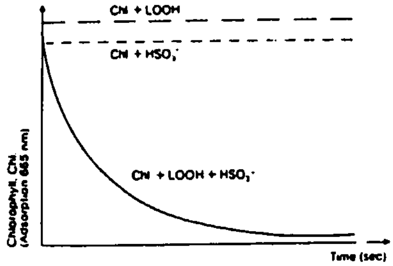


FIGURE 2 Atmospheric interactions (simulation) during photosmog production.[1]



$$HSO_3^- + LOOH \longrightarrow LO^\cdot + HSO_3^\cdot + OH^-$$

$$LO^\cdot + HSO_3^- + H^+ \longrightarrow HSO_3^\cdot + LOH$$

$$LO^\cdot + \text{Chlorophyll} \longrightarrow \text{cooxidation}$$

$$2HSO_3^\cdot + H_2O \longrightarrow SO_4^{2-} + HSO_3^- + 3H^+$$

$$HSO_3^\cdot + O_2 + H_2O \longrightarrow SO_4^{2-} + O_2^{\cdot -} + 3H^+$$

FIGURE 3 Chlorophyll degradation by HSO_3^- and peroxide.[4]

As shown later HSO_3^- also interacts with particulate systems such as asbestos fibres and diesel soot.

O_3

Ozone specifically adds onto double bonds forming the Criegee-Zwitter-ion and finally hydroperoxides[5] (Figure 4).

NO_2

Since NO_2 is a radical by itself, its addition onto double bonds again yields free

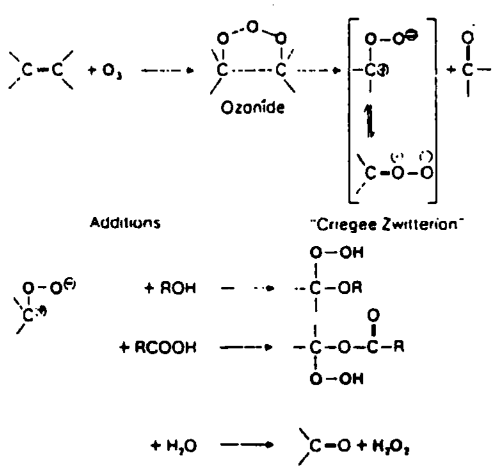


FIGURE 4 Reaction of ozone with C = C double bonds.

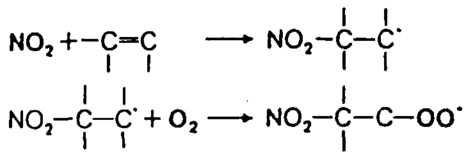


FIGURE 5 Formation of peroxides by NO_2.

radicals, which add oxygen yielding hydroperoxyl radicals, which in turn can initiate chain reactions (Figure 5). Furthermore in aqueuos media NO_2 also can produce biphenols through oxidation of tyrosine groups in peptides and proteins, thus yielding higher aggregates.[7]

PAN

PAN and other organic peroxides react with different biomolecules such as amino-acids and SH-groups. Especially strong effects on the indole metabolism have been measured. Indolacetic acid (IAA), a plant hormone, is converted into 3-hydroxy-methyloxindol (HMO) which is actually a growth inhibitor.[8]

These examples are anything but all possible reactions with molecules in living cells we could think of. Physiological reaction partners and the corresponding reactions of different air pollutants are listed in Table II.

EFFECTS OF CHEMICAL STRESS ON PLANT SYSTEMS

An almost exhausting review about effects of air pollutants and their combinations on plants has recently been given by Darrall (1989).[10] One of the most important results of his comparative studies is the general observation, that mixtures of gases such as $SO_2 + O_3$, $SO_2 + NO_2$ or $O_3 + NO_2$ principally seem to lower the threshold doses for the single components. As another general principle, both very low and very high light intensities enhance the toxic effects due to either lack of repair "energy" or additional "light stress". As most important physiological parameters she compares

TABLE II
Examples for phytotoxic effects of aerosol contents (after ref.[1])

compound	reaction partner	physiol. react. partner	symptoms
SO_2, HSO_3^-	peroxides, thioles	membranes, enzymes	inhibition of PS, necrotic spots
NO_x	alkenes	membranes, enzymes	— (growth inhibition)
O_3	alkenes, thioles	membranes, enzymes, hormones, nucleic acids	flecking, bleaching, membrane leaks
PAN	thioles, amines, acrylic compounds	methionine, indoles, amino acids, hormones	inhibition of growth necrotic reactions

the effects on photosynthesis, respiration, carbon partitioning and stomatal functions. A summary of these principal results is given in the following.

EFFECTS ON PHOTOSYNTHESIS

SO_2

The lowest concentrations where responses are observed, are between 200 and 400 ppb (1 ppb = 2,67 $\mu g/m^3$). Fast recoveries from inhibitions are observed after finishing the influence of the stressor.

O_3

Lowest concentrations of stress responses are in the proximity of 100 ppb for one hour or intermittently of 35 ppb over 147 hours within three weeks (1 ppb = 2 $\mu g/m^3$).

NO_2, NO

Effects are only visible at very high concentrations above 500–700 ppb (1 ppb = 1.9 $\mu g/m^3$).

Combinations of SO_2 and O_3, O_3 and NO_2, generally lower the indicated threshold values or increase the severity of symptoms. Highly polluted areas may contain up to 1000 $\mu g/m^3$ SO_2, 300 $\mu g/m^3$ O_3 and several thousand $\mu g/m^3$ NO_x for short times.

EFFECTS ON STOMATAL APERTURES

At low doses of SO_2, O_3 or NO_x stomatal aperture is increased. These doses are mostly below 100 ppb. High doses of SO_2 (> 1900 ppb) O_3 (> 200 ppb), NO_2 (> > 200 ppb) or NO (> 1000 ppb) yield stomatal closure. Combinations of low doses either have no effect or prevent the opening process. Sometimes they also yield closure. Interactions with water stress (dryness) induce different responses. The resistance against O_3 is increased. Since it is known that O_3 penetrates the leaves exclusively through the stomata and then is rapidly degraded in cell walls or plasmalemma the actual concentrations in the intercellular spaces is quasi zero.[10] Thus stomatal closure prevents O_3 effects. SO_2 and NO_2 or other air pollutants change the consistence of cuticular waxes and increase water fluxes. Especially the wax covers over stomates are impaired increasing the sensitivities towards infections and water losses.[9,12]

DIFFERENCES IN CARBON PARTITIONING

Treatment with SO_2 (> 40 ppb) over nine weeks or O_3 (> 50 ppb) over 40 hours within five weeks reduces carbohydrate transports into the roots, yielding a disturbed dry-weight balance. Assimilates seem to be accumulated in the leaves resulting in weight losses in the root system. Therefore the activity of the root system and in consequence the tolerance against dryness is rapidly lowered. Responses to water stress are enhanced as the result of a disturbed carbohydrate distribution.

TABLE III
Ascorbic acid and glutathione contents in correlation to chlorophyll of spruce needles (after ref.[3])

year	84 h	84 b	83 h	83 b	82 h	82 b	year	82 h	82 b	81 h	81 b
Chlorophyll (mg/g dw)	2.2	2.0	2.7	1.7	3.2	0.76	Chlorophyll (mg/g dw)	3.3	0.7	2.9	1.4
Asc.	1.97	4.4	3.9	5.1	5.55	7.7	Asc. (mg/g dw)	4.6	6.2	4.4	7.8
Dehydroasc.	0.39	1.0	0.3	0.8	0.06	0.3	Dehydroasc. (mg/g dw)	0.6	0.6	0.2	2.0
GSH	51	84	46	104	84	203	GSH (mg/g dw)	57	120	41	202

h = healthy; b = bleached or light green

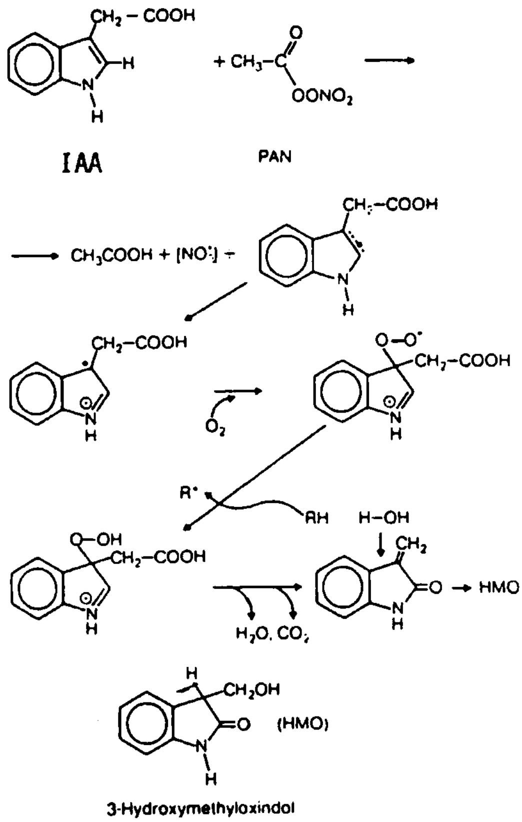


FIGURE 6 Oxidation of IAA by PAN: tentative reaction mechanism.[9]

INFLUENCE ON RESPIRATION

Dark respiration is enhanced by SO_2 as well as by O_3, while NO_2 has little or no effects. High concentrations of SO_2 and O_3 (> 900 ppb) inhibit photorespiration.

Physiological aspects of plant damage by air pollutants are given by Heath[13] (1980) and effects on productivity have been reviewed by Laurence and Weinstein[14] (1981). Furthermore a symposium review with the title: "Air pollution and plant metabolism" has recently been published.[15]

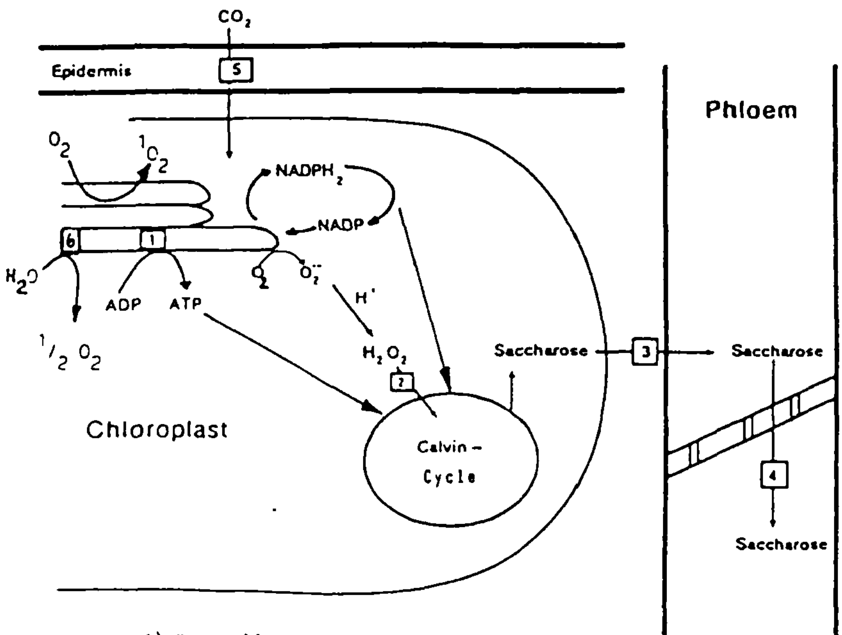
EFFECTS ON ANTIOXIDATIVE SYSTEMS

Treatment of spinach leaves with ozone in the light yields malonedialdehyd as chlorophyll and carotenoids are degraded. Exogenous applications of SOD or ascorbate diminuate the noxious effects indicating a contribution of superoxide during ozone-dependent damage.[16]

Treatment with air pollutants increases the endogenous antioxidative potential. Tanaka and Sugahara[17] found an increase of SOD activity after SO_2 treatment.

Peroxidase and SOD were increased, ascorbate however was decreased in spruce (4 years old) after ozone treatment.[18] Similar observations had been made by Mehlhorn *et al.* 1986[19] and Guderian *et al.* (1988),[20] who also treated conifers with SO_2/O_3^+ combinations. In all cases superoxide dismutase and peroxidase were increased. In addition to these enzymic changes ascorbate, glutathione and α-tocopherol were also increased as compared to the controls. Spruce-needles from damaged and healthy looking trees also reveal differences in superoxide dismutase: SOD is generally increased in partially bleached needles whereas catalase is significantly decreased, following decreasing chlorphyll contents.[12] With decreasing chlorophyll contents ascorbate and glutathione are generally increased[3] (Table III).

Ozone damage in tobacco (Mutant Bel W-3) was prevented by treatment with aqueous polyamines (putrescine-, spermidine-, spermine-solutions), although these compounds are not good radical scavengers.[21] Parallel to these findings it is interesting to note that O_3 specifically inactivates cell wall-associated diamine oxidase, while no influence on peroxidase was observable.[22] The mechanism of polyamines protecting from ozone damage is not yet understood. It is known that H_2O_2 induces several resistance processes[23] including formation of enzymes important for phytoalexine synthesis. Polyamines are oxidized in the cell walls yielding H_2O_2, on the other hand. Thus, a possible involvement of H_2O_2 in message transfer by the cell walls might be seen. The production of phytoalexines in soy beans by O_3 treatment has already been reported by Keen and Taylor in 1975.[24]



Blocks: 1) Uncoupling
2) Calvin cycle enzymes (F-6-Pase,S-7-Pase),inhibited by hydrogen peroxide
3),4) Carbohydrate translocation, transport-antiport;
5) Stomatal aperture
6) Photoinhibition, electron transport,photosystem II;

FIGURE 7 Induction of photodynamic destructions by metabolic blocks in higher plants.

The biochemical consequences of stress influences have been shown to include stomatal aperture as well as carbon distribution in the plant. Several stressors like water deficiency, osmotic changes, high salt concentrations or radiation (UV), temperature changes or high light intensities are responded in the higher plant by specific reactions or symptoms. One general effect is, that plants show higher light sensitivity probably due to lack of energy dissipation through photosynthtic electron transport. Processes involved in these reaction chains have recently been reviewed by Elstner *et al.* 1988.[25] This "stress feedback chain" increases the amount of excited pigments visible as an increased fluorescence yield. Increased chemiluminescence of stressed tissue, lipid breakdown products such as MDA and increased ESR-activity have also been reported. All these indicators support the notion that radical chains are induced by stressors. In the thylakoid system both formation of superoxide, H_2O_2 and singlet oxygen has been described.[26] A generalized scheme indicating the mentioned processes is given in Figure 7.

The consequence of decreased NADPH oxidation and ATP utilization is an increased electron transport to oxygen and thus an increase of photorespiratory sequences. As next avoidance and tolerance reactions by rearrangements in the photosystems are indicated.[27] As a final consequence singlet oxygen production in the photosystems initiates degradation of unsaturated fatty acids measurable as malondialdehyde production and ethane release. In the early stages ethylene formation is a rapid indicator of induction of stress situations.[28,29] In this context it is interesting to note that both ethane release from linolenic or other "omega minus three" fatty acids as well as ethylene release from 1-aminocyclopropane-1-carboxylic acid (ACC) are oxygen-dependent processes. Finally loss of control is visible as degradation of singlet quenchers like carotenoides, flooding with peroxides and thus inactivation of Calvin cycle enzymes (FDPase, SBPase) and decay of catalase. Membranes are peroxidized measurable as ion leaks. The last step is necrosis and cellular death.

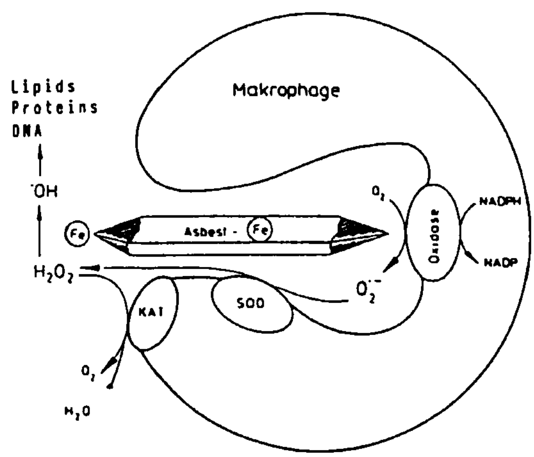


FIGURE 8 Cooperative effects between asbestos fibers and macrophages: an hypothesis based on biochemical models.[30]

Medical Aspects

All mentioned gases, SO_2, NO_2, O_3, as well as particles have negative effects on human helth. In this context especially cigarette smoking should be mentioned.[30,31] Ozone effects had intensively been studied by Dooley and Mudd,[32] Peters and Mudd[33] and Knight and Mudd.[34] Effects on several compounds like tryptophane have been observed. Enzymes with SH-groups were especially influenced. Since ozone secondarily yields OH-radicals and hydroperoxides, reactions of ROO˙ and RO˙ have to be considered. The different reactivities of ROO˙ and RO˙ have recently been well documented by VanderZee *et al.* (1989), showing that GAPDH is damaged by BuOOH, while ADH and acetylcholinesterase are especially inactivated by BuO˙ and lysozyme, LDH and acetylcholinesterase specifically by BuOO˙ (Bu = tert.butyl). Different types of smoke and especially cigarette smoke interact with NO_2 where finally nitroaromatic and aliphatic compounds are produced, which are mutagenic and carcinogenic. A mutagenic (DNA strand breaks) effect of a combination of cigarette smoke and asbestos has recently been documented by Jackson *et al.*, (1987).[36]

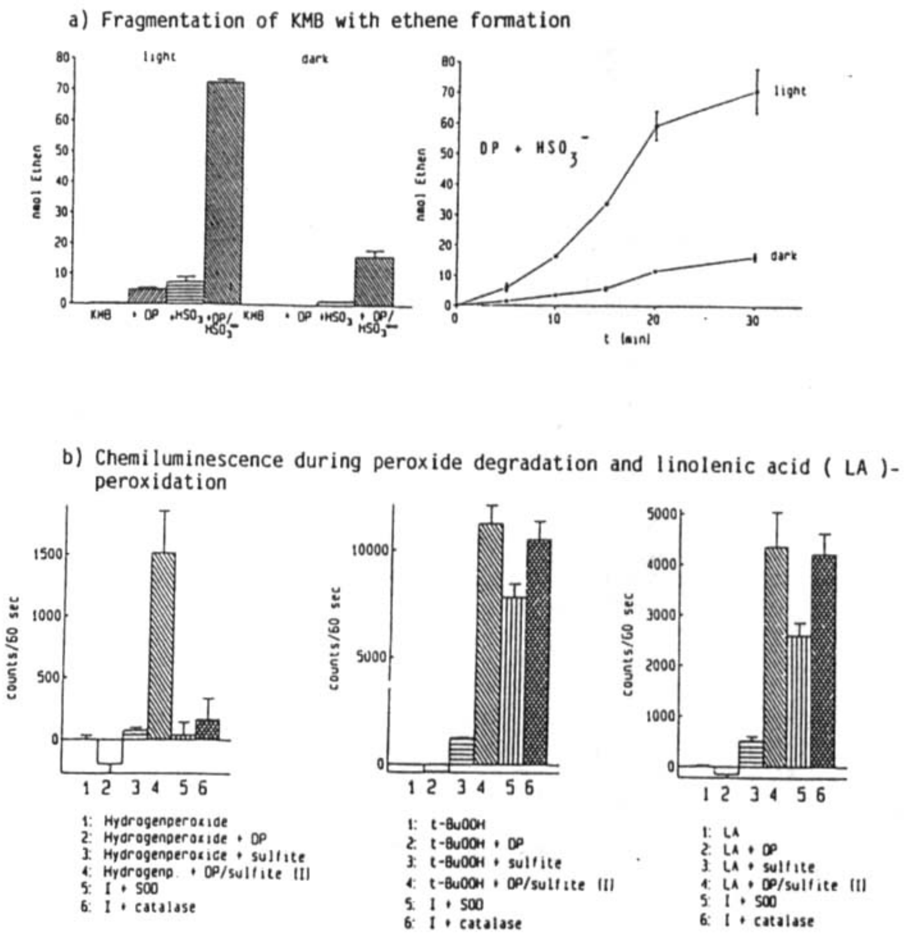


FIGURE 9 Biochemical activities of diesel particles (DP) in cooperation with bisulfite.[41]

NO_2 and O_3 in combination have been reported to influence xenobiotic-metabolizing activities in rat lungs.[37] Oxygen activating activities of asbestos fibers, which operate similar to Fenton oxidants and destructive effects of diesel particles have also recently been described in more detail, where especially cooperative effects with SO_2 have been observed.[38-41] A summary of biochemical parameters observed with asbestos fibers and diesel particles is given in Figures 8 and 9.

CONCLUSIONS

As conclusion we can say that activated oxygen species are involved during the transformation of air pollutants as well as in several reactions in the living cell where primary reactions of the air pollutant or its conversion products are followed by secondary reactions. As final reactants hydroperoxides and alkoxyl- or peroxylradicals have to be considered. In plants as well as in animal cells transport processes are affected in the first line. Depending on the air pollutant and the doses specific metabolic reactions or enzyme-activities are influenced. Interactions between several air pollutants seem to decrease threshold levels thus extremely complicating experimental approaches and predictions. In the near future mankind will have to spend increasing amounts of money and effort to prevent air pollution and/or its effects.

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