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Chemistry and Physiology of Los Angeles Smog

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Air pollution in the Los Angeles area is characterized by a decrease in visibility, crop damage, eye irritation, objectionable odor, and rubber deterioration. These effects are attributed to the release of large quantities of hydrocarbons and nitrogen oxides to the atmosphere. The photochemical action of nitrogen oxides oxidizes the hydrocarbons and thereby forms ozone, responsible for rubber cracking. Under experimental conditions, organic peroxides formed in the vapor phase oxidation of hydrocarbons have been shown to give eye irritation and crop damage resembling closely that observed on smog days.

AIR pollution in the Los Angeles area is characterized by a decrease in visibility, crop damage, eye irritation, objectionable odor, and rubber deterioration. Although dust and fumes were materially reduced through the combined action of the Los Angeles County Air Pollution Control District and the industries located in the area, the smog conditions were not alleviated proportionally. A program studying the chemical aspects of air pollutants was started at the Air Pollution Control District, and its efforts were combined with those of the California Institute of Technology. It was found that the most characteristic property of the Los Angeles air during smog periods was the oxidizing capacity demonstrated in the release of iodine from neutral buffered potassium iodide solutions.

Condensates of smog air collected by passing air through traps cooled to -80° and -180° C. showed the same oxidizing action. This iodine release could not be explained by the very small amounts of metal oxides present, and only partially by the presence of nitrogen oxides. The conclusion was drawn that peroxides of organic nature were present, which could originate in oxidation of organic material in the air by other air constituents such as ozone and nitrogen oxides (6), and it was demonstrated that the vapor phase reactions of ozone and nitrogen oxides with unsaturated hydrocarbons produced aerosols of eye-irritating properties. When a cracked gasoline was used as a source of olefins, aerosols were produced which also simulated the odor usually associated with smog (5).

DETERMINATION OF OZONE AND PEROXIDES IN AIR

Evidence that these reactions play a role in the Los Angeles smog problem came from the study of rubber cracking and crop

The aerosols formed in these oxidations are contributors to the decrease in visibility. The odors observed in oxidation of gasoline fractions are similar to those associated with smog. Hydrocarbons present in cracked petroleum products, harmless in themselves, are transformed in the atmosphere into compounds highly irritating to both plants and animals, and should therefore be considered as potentially toxic materials. A proper evaluation of the contribution of air pollutants to the smog nuisance must include not only the time and place of their emission, but also their fate in the air.

damage in this area. It has long been known that ozone has a characteristic cracking action on raw or vulcanized rubber when rubber is under strain in a bent or stretched condition (3). Low concentrations of ozone are used commercially for comparative aging tests on rubber compounds, but when a standardized rubber is used, this method can serve as a sensitive measure of ozone concentration (2). By comparing the time necessary to obtain just visible cracking, it was noticed that under smog conditions the minimum cracking time was reduced sharply. Whereas normally 45 minutes are necessary to observe this effect, severe smog conditions reduced the cracking time to only 6 minutes. These times correspond to the action of 0.03 and 0.22 p.p.m. of ozone, respectively. In this case, the cracking time was determined every hour, and the results were plotted in ozone concentrations which would give the same response (Figure 1). The sharp rise corresponds closely to the subjective judgment of the severity of the smog.

The presence in smog air of strong oxidizing agents closely resembling ozone in its action on organic compounds could be expected to lead to the formation of peroxides and their degradation products. In the determination of the peroxidic reaction products in the air, chemical methods are not suitable because of the presence of other oxidants and reducing substances, and advantage was therefore taken of the specificity of enzymatic reactions (9). The enzyme peroxidase, in the presence of hydroperoxide groups, catalyzes the oxidation of phenols and amines to colored derivatives. The oxidation of guaiac tincture produces a blue color which can be measured colorimetrically. No color appears when the enzyme is poisoned with small quantities of hydrogen cyanide (16). This inhibition effect distinguishes

peroxides from oxidation agents such as nitrogen dioxide and ozone, which produce a color regardless of the presence of hydrogen cyanide.

The peroxidase test was run on an hourly basis simultaneously with the rubber cracking test. A sudden increase in the color formation was noticed when the smog wave arrived in Pasadena. At the same time a separate test with addition of hydrogen cyanide to the bubblers showed a considerable reduction in color formation as indicated in Figure 1, B. This proved that the strong increase in coloration was due to peroxides and not to nitrogen oxides or ozone. A comparison of the two curves shows that the bluing of guaiac tincture persisted longer than the cracking of rubber. This phenomenon is readily explained when it is realized that the peroxides are the products resulting from the action of the oxidant which is consumed in the oxidation process.

CROP DAMAGE

An important contribution to the understanding of the chemistry of the Los Angeles smog was made by the study of crop damage, a cooperative enterprise of the Los Angeles County Air Pollution Control District, the California Institute of Technology, and the University of California. For the determination of the crop-damaging materials present in the air, five different plants—spinach, beets, endive, oats, and alfalfa—were used. The smog symptoms on these indicator plants are well known through previous studies (11). The production of a metallic sheen on the lower surface of leaves on spinach, sugar beets, and endive, especially, distinguishes this damage from the effect of previously known toxic materials. None of the usual inorganic pollutants, such as sulfur dioxide, chlorine, hydrogen sulfide, or hydrogen fluoride, were found to be present in the smog atmosphere in quantities likely to cause damage, except in the immediate neighborhood of the emission.

After testing a series of pure compounds of organic nature found or suspected of being in the air, and failing to produce the smog symptoms, attention was given to the reaction products which are formed in the air from natural components and air pollutants, as well as from the air pollutants themselves.

In view of the strong oxidizing action of the smog atmosphere and the suspected presence in the air of considerable amounts of easily oxidizable material from petroleum products, fumigations were carried out with ozone and vapors of a cracked gasoline containing 20% unsaturates. The development of the damage symptoms such as oiliness of the underside of the leaves of spinach and endive after a few hours of fumigation, as well as the further development of the symptoms on all five indicator plants, was indistinguishable from that noticed on plants exposed to smog. In these experiments the ozone concentration was adjusted to 0.2 p.p.m., which corresponds to the degree of rubber cracking found during intense smog conditions. In order to eliminate the bleaching effects on the test plants which could possibly result from unreacted ozone, the hydrocarbon was held in excess at 4 to 5 p.p.m. This excess of hydrocarbon has no effect on plants. Determination of the reaction products—peroxides, acids, and aldehydes—showed that no more olefin is oxidized than corresponds to the ozone supplied. These findings are in agreement with quantitative ozonolysis experiments carried out by Dallwig and Briner (4). The effective concentration of the hydrocarbon is therefore the same as that of the ozone before hydrocarbon is admitted and could not exceed 0.2 p.p.m. in these experiments.

In an effort to establish the nature of the agent responsible for the damaging effects, the gasoline was distilled in 10° C. fractions, and these were released in the fumigation room together with ozone (0.2 p.p.m.). Maximum damage was obtained with the fraction boiling between 39° and 69° C. These results are presented in Figure 2, A, in which the estimated degree of damage is plotted against the average boiling point of the gasoline fractions used in the fumigation. A determination of the olefin content of the fractions shows that the maximum of plant damage coin-

cides with the fraction of highest unsaturation (Figure 2, D). Although the olefin content of the fraction is a prerequisite for the ozone action, the unsaturation of the fractions could not be the sole reason for this coincidence, since the majority of the fractions used contained more olefin than was required for the consumption of the available ozone. That the size and structure of the olefin plays an important role was shown by fumigation with ozone

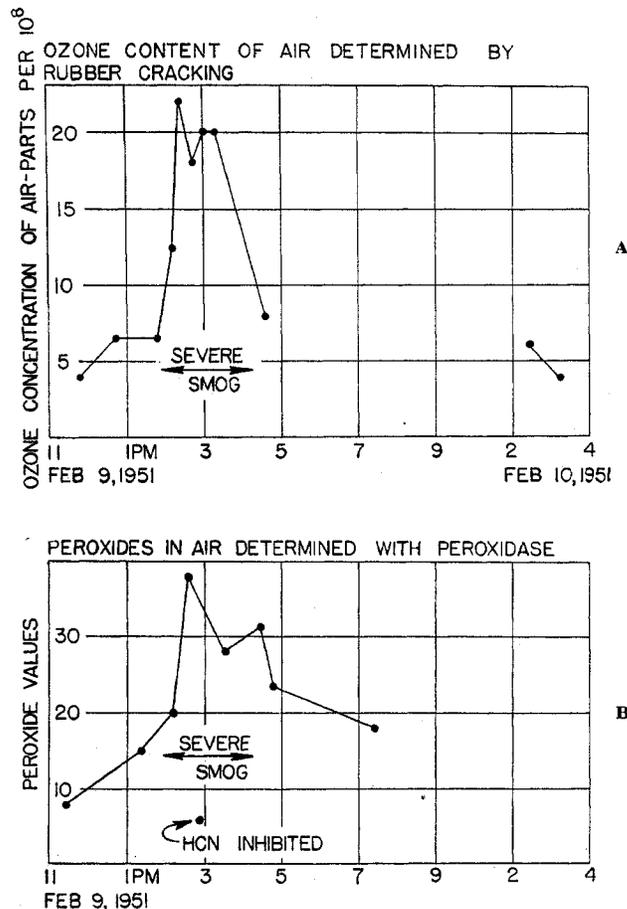


Figure 1. Comparison of the Hourly Fluctuation of Rubber Cracking and Peroxide Content of Air on a Smog Day

- A. Rubber cracking during day of severe smog
B. Peroxide content as determined with peroxidase and guaiac tincture during the same day

and a series of pure olefins. This series consisted of straight-chain olefins, ranging from C_2 to C_{14} with end methylene groups. To show the close agreement between these experiments and those with gasoline fractions, the severity of the typical crop damage is plotted against the boiling points of the pure olefins on the same temperature scale as was used in the case of the gasoline fractions (Figure 2, B). Maximum effects were obtained by using olefins with 5 and 6 carbon atoms with the double bond in the end position. However, the end position of the double bond is not essential, since 3-heptene, 4-nonene, and cyclohexene gave typical smog damage upon ozonization. The activity of the oxidation products of isobutene shows that the branched-chain isomers of the olefins must be included in the series of toxic agents. The optimum activity of the C_5 and C_6 series is attributed to the stability of the intermediate products in the reaction process. The ozonides of propene and the normal butenes rapidly decompose to form the corresponding inactive aldehydes and acids. The reactivity of the ozonides of olefins decreases with increasing car-

bon number, which could furnish the explanation of the lack of toxic effect of higher olefins such as decene and tetradecene.

For the ozonization products of 1-hexene, the threshold value for plant damage was determined. With a peroxide concentration of 0.01 p.p.m., slight but typical damage resulted. The concentration of ozone before admittance of the hydrocarbon necessary to obtain this peroxide concentration was 0.05 p.p.m. This figure is well within the range of zone concentrations found in smog air.

A representative higher aldehyde (*n*-valeraldehyde) and a higher acid (*n*-valeric acid) did not show damage at a concentration of several parts per million. Hydrogen peroxide, a possible degradation product in the hydrolysis of the ozonides, failed to show any effect on the plants in concentrations of 1 p.p.m. Since the end products of the ozone degradation of the olefin—the aldehydes, acids, and hydrogen peroxide—are not responsible for the plant damage, the active agents must be found in the highly oxygenated organic compounds of peroxide nature formed as intermediates.

Under the influence of sunlight, nitrogen dioxide, dissociating into nitric oxide and atomic oxygen, readily oxidizes a number of compounds. Nitric oxide is then oxidized by molecular oxygen to nitrogen dioxide, which functions therefore as a continuous source of atomic oxygen. In view of the positive results of the ozone oxidation experiments, it was of interest to see if, with the help of this catalytic oxidation, plant damage could be produced with hydrocarbons. The nitrogen oxide concentration reaches values of 0.4 p.p.m. in the Los Angeles area, and this level was therefore adopted in the fumigation experiments. Again using gasoline as a source of hydrocarbons and 0.4 p.p.m. of nitrogen dioxide, it was seen that the precursors of the damaging factors are in the same fraction which gave typical damage in the ozone oxidation experiments. It was found that these effects are not due to the action of nitrogen dioxide by itself, with or without ultraviolet light, nor to the action of the hydrocarbons with sunlight. Although gasoline and also 1-hexene with nitrogen dioxide gave plant damage when irradiated with sunlight or ultraviolet light, no effects were found when weak fluorescent light (1600 foot candles) was used. In the sunlight, the oxidation of the olefin takes place, whereas in the dark or in weak artificial light the formation of nitro compounds predominates. Since alcohols, aldehydes, and acids under the influence of the catalytic oxidation with nitrogen dioxide and sunlight did not show any damage to plants, the conclusion that intermediate peroxide compounds formed from the olefins are responsible for the typical plant damage is reached in this case also.

EYE IRRITATION

During the plant experiments with fractions of gasoline and also with pure olefins and ozone, frequent eye irritation was observed. To study those reactions further a fumigation room was built from Plexiglas, which permits the use of practically the entire spectrum of the sun available to the lower regions of the atmosphere. When a cracked gasoline was released in the presence of nitrogen oxides and sunlight, characteristic smog odor and eye irritation were soon apparent. In order to determine the nature of the hydrocarbons, which upon oxidation are responsible for the eye irritation, 10° C. fractions of gasoline were used, while the concentration of the oxidant was adjusted to 0.4 p.p.m. of nitrogen dioxide and 0.2 p.p.m. of ozone. After the hydrocarbon had been admitted, the total oxidant concentration as measured by iodine release from buffered potassium iodide solution was 0.7 p.p.m., closely resembling the oxidizing action of severe smog, when 0.6 p.p.m. was found.

Observers sensitive to eye irritation on smog days compared their reaction in these fumigations with those experienced under conditions of natural smog. When 10 p.p.m. of hydrocarbon were used, irritation was pronounced in the boiling point region from 35° to 90° C., and was noticeable over a far wider range. In experiments with concentrations of 1.6 p.p.m., the eye irritation was definite in the range of 50° to 80° C. and in the fractions boiling below 35° C. as shown in Figure 2, C. Experiments with 0.4 p.p.m. of nitrogen dioxide and fractions of gasoline without the addition of ozone gave similar results. A comparison of Figures 2, A and 2, C shows maximum plant damage and eye irritation to occur in about the same boiling point region of the gasoline fractions. Eye irritation is, however, observed also in fractions with boiling points below 35° C.

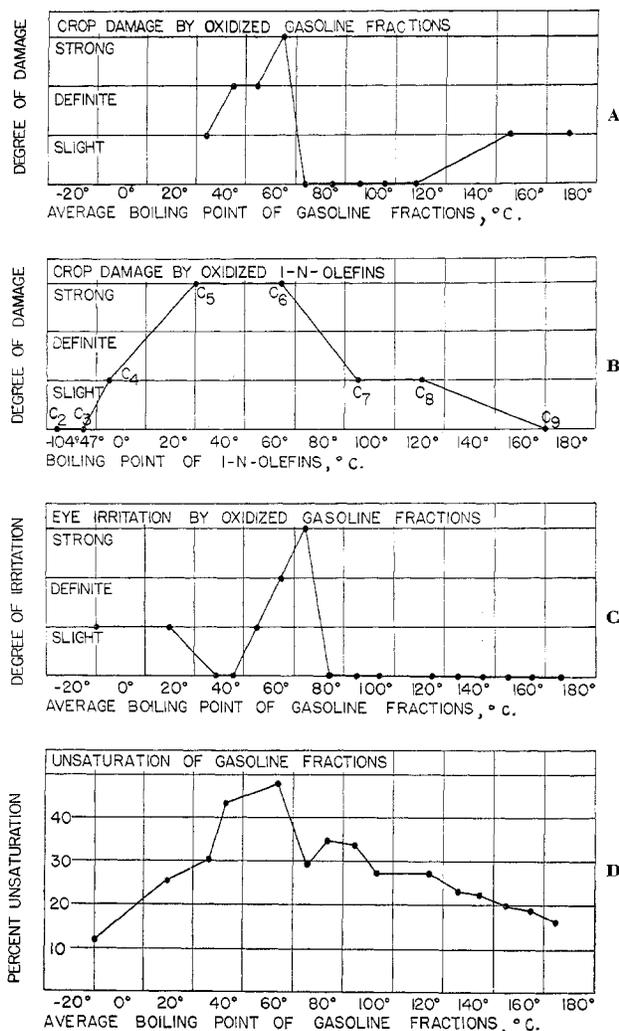


Figure 2. Comparison of Results of Crop Damage and Eye Irritation Experiments with Olefin Content of Gasoline Fractions

- A. Crop damage from oxidized gasoline fractions (5 p.p.m.) with 0.2 p.p.m. of ozone
- B. Crop damage from oxidized *n*-olefins (5 p.p.m.) with 0.2 p.p.m. of ozone
- C. Eye irritation from oxidized gasoline fractions (1.6 p.p.m.) with 0.4 p.p.m. of nitrogen dioxide, 0.2 p.p.m. of ozone, and sunlight
- D. Unsaturation in percentage of 10° C. fractions of a cracked gas line used in the experiments of A and C

In fumigation experiments of this kind a variety of oxidation products is formed. The primary product, the ozonide, itself a peroxide, undergoes a series of changes leading to hydroxy- and aldehyde peroxides, and finally to aldehydes, ketones, and organic acids. These end products formed from the physiologically active hydrocarbons do not occur, even after complete conversion of the ozonides, in such high concentrations that damage could be attributed to their formation. Threshold values determined for formic acid and formaldehyde are, respectively, at 1 and 2 p.p.m.

These experiments were followed by a similar series of oxidation reactions using pure olefins as sources of hydrocarbons, and the results are listed in Table I.

Definite smog effects can be obtained using concentrations of 0.2 p.p.m. of 1-butene and 0.5 p.p.m. of 2-butene. These observations are in harmony with the observed action of the lower boiling fractions of gasoline. These fractions are not active in the crop damage, and although the principle in the action of the irritation on plants and animals is considered to be the same, this difference may, perhaps, be explained by the instability of the peroxidic oxidation products of olefins with four and less carbon atoms and to the differences in the manner of contact and the structure of the tissues involved.

TABLE I. EYE IRRITATION OBSERVED IN THE OXIDATION OF OLEFINS

(With 0.4 p.p.m. of nitrogen dioxide and 0.2 p.p.m. of ozone under influence of sunlight)

Olefin	Hydrocarbon Concentration, P.P.M.	Degree of Eye Irritation
Ethylene	1	Doubtful
Propene	1	None
1-Butene	3	Severe smog
1-Butene	0.5	Severe smog
1-Butene	0.2	Light smog
2-Butene	3	Medium smog
2-Butene	1	Medium smog
2-Butene	0.5	Medium smog
Isobutene	1	None
1-Hexene	1	Medium smog

As in the crop damage experiments, the end products of the oxidations—aldehydes and acids—cannot be responsible for the physiological action since their concentrations are considerably lower than that required for irritation. Formaldehyde can only be a contributing factor to the eye irritation in some cases where end methylene groups are present. Analytical data on formaldehyde, found in the Los Angeles area in concentrations of 0.04 to 0.09 p.p.m., several times below its irritation threshold, confirm the secondary role of this compound as smog irritant. The severe smog effect attained with 2-butene, which would not furnish formaldehyde upon oxidation, supplies additional evidence that not the end products of the oxidation but intermediate stages, of peroxidic nature, are responsible for the irritation.

AEROSOL FORMATION

It has been noticed in the fumigation experiments that the vapor phase oxidation of olefins is always accompanied by aerosol formation. In the crop damage studies with ozone and hydrocarbons the reactants were allowed to combine at high concentration, and the oxidation products, leaving the reaction tube in the form of a dense smoke, were then dispersed in the room. In the experiments in the Plexiglas room using nitrogen dioxide and sunlight, with or without the addition of ozone, for the oxidation of the hydrocarbons, the reactants were introduced separately. In both cases, reduction of visibility can be observed. These effects are especially noticeable with ring compounds having a double bond in the ring, such as cyclohexene, indene, and dicyclopentadiene. In these cases the opening of the ring will yield practically nonvolatile oxidation products. Because of the introduction of several polar groups, the volatility decreases so radically that aerosol formation is inevitable. The well-known polymerizing action of peroxides formed in the oxidation process might well be an additional factor in the formation of nonvolatile products.

A striking demonstration of haze formation through the oxidation of hydrocarbons with nitrogen oxides and sunlight can be given by using dicyclopentadiene or indene in a concentration of 50 p.p.m. In a few minutes a dense blue haze develops, obscuring vision over a distance of only 8 feet. At a concentration of 10 p.p.m. of hydrocarbon, the blurring of objects is already notice-

able over this short distance. Similar observations have been made on the oxidation of gasoline fractions.

Several investigators have reported that a considerable portion of the droplets collected from smog are of oily nature, and chemical analyses have shown that their composition resembles that of droplets found in the artificially produced aerosols of oxidized hydrocarbons (10, 13, 14). The large tonnage of hydrocarbons released into the Los Angeles atmosphere and the presence of cyclenes in catalytically cracked petroleum products are additional reasons for thorough measurements on this type of aerosol formation to determine the role of those oxidation and polymerization products in the reduction of visibility during smog periods.

SMOG CONSTITUENTS

Parallel with the physiological investigations, the analytical work carried out on samples of pollutants collected on filters and in bubblers has shown the presence of the more stable end products—aldehydes and organic acids—of the previously mentioned reactions. Chromatographic separation of the *p*-phenylphenacyl derivatives of the acids gave evidence of the presence of at least 15 different organic acids, identification of which is still in progress (10). In the hands of Shepherd, the mass spectrograph gave valuable information on the multitude of hydrocarbons present in the Los Angeles air. In addition, he was able to show the similarity of the mass spectrograms from mixtures of hydrocarbons oxidized with ozone, nitrogen oxides, and ultraviolet light and those recorded from smog (12). Estimates, as well as actual measurements, have shown that from 1000 to 2000 tons of hydrocarbons are released daily into the Los Angeles atmosphere through evaporation losses in the manufacture and distribution of petroleum products and through incomplete combustion, chiefly from automobiles (10). Combustion processes add nitrogen oxides at a rate of 200 to 300 tons daily to the air.

FORMATION OF OZONE

While, therefore, the ingredients for the production of crop damage and eye irritation are available in the polluted air, the presence of excess of oxidant as measured by iodine release from neutral buffered potassium iodide solution requires explanation. This excess oxidant, calculated as ozone, amounts to 0.5 to 0.6 p.p.m. on severe smog days.

A large part of this iodine release is due to the presence of nitrogen oxides, which, in concentrations at which they occur in the Los Angeles area, oxidize neutral buffered potassium iodide solutions. The more puzzling fraction of the so-called total oxidant in smog is that which closely simulates the behavior of ozone in giving typical rubber cracking. This fraction was shown to rise during severe smog, and in the standardized rubber cracking test mentioned earlier, cracking times of 6 minutes were observed, corresponding to an ozone concentration of 0.22 p.p.m. The natural ozone concentration on the earth's surface is reported to be of the order 0.02 to 0.03 p.p.m. These values were confirmed in this work, using the rubber cracking test in unpolluted desert and beach areas. It is unlikely that additional ozone could be drawn from the higher atmosphere when the presence of inversion conditions characteristic for smog conditions prevents this free exchange. Further evidence against such a possibility is presented by the nearly complete absence of rubber cracking at night. This observation points to photochemical processes in the formation of the rubber cracking material.

It was thought that the photochemical dissociation of nitrogen oxides, forming atomic oxygen and possibly ozone, could be the main cause of the rapid rubber cracking. However, recent experiments have shown that this reaction is more complex (?). Rapid rubber cracking comparable to that observed during smog periods was observed during the plant fumigations with nitrogen oxides and sunlight only in the presence of organic material such as hydrocarbons. When gasoline fractions are used in concentrations of 0.1 to 1.0 p.p.m. in the presence of 0.4 p.p.m. of nitrogen

dioxide, optimum cracking occurs in the same boiling point region where the most intense crop damage had been found. This effect on rubber was confirmed by the use of branched, saturated hydrocarbons and olefins as well as their oxygen derivatives—alcohols, aldehydes, ketones, and acids. In the photochemical oxidation of 3-methylheptane and also of diethylacetic acid with nitrogen oxides, the rubber cracking material was isolated by fractional condensation. The condensate, freed from nitrogen oxides and peroxides, was identified as ozone.

The concentration of ozone produced during a few hours of irradiation exceeds that of the nitrogen oxides or organic compounds used. A chain mechanism is therefore postulated in which, probably, free radicals play a role in the transfer of an oxygen atom to an oxygen molecule. This view is supported by the rubber cracking observed with butyl nitrite and also with diacetyl and sunlight in the absence of nitrogen oxides. It is known that in both cases free radicals form upon exposure to light (1, 15). When these reactions were carried out in the presence of air, the formation of ozone was established by isolation and chemical identification.

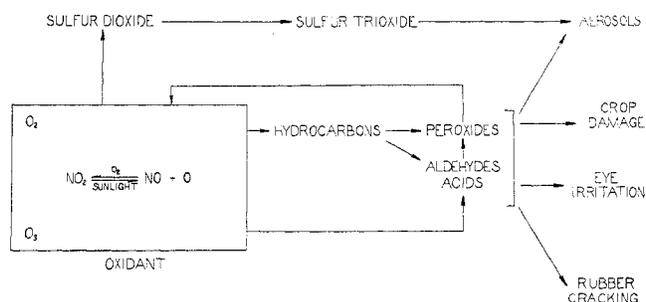


Figure 3. Schematic Presentation of Reactions in Polluted Air Leading to Smog Symptoms

Since the concentrations of the materials used in the photochemical oxidations with nitrogen oxides were of the same order of magnitude as those found in the smog atmosphere, the abnormally high ozone content and consequent severe rubber cracking during such a period is readily accounted for by the ozone formed in these reactions. The action of ozone is naturally not limited to the attack of rubber but is responsible for the oxidation of other olefins as well.

SUMMARY

On the basis of these experiments, it is possible to condense the major features in the development of irritating and nuisance effects in the Los Angeles atmosphere as shown in Figure 3. The oxidant is represented by a complex of factors consisting of oxygen, atomic oxygen formed by the photochemical dissociation of nitrogen dioxide, and ozone produced in the photochemical oxidation of organic material. The oxidant reacts with hydrocarbons and their oxidation products, producing peroxides and further degradation products. The arrow leading from the peroxides to the oxidant indicates the participation of these compounds or their radicals in the formation of ozone and in the acceleration of oxygen uptake and shortening of the induction period in the oxidation of hydrocarbons (17).

This scheme includes the oxidation products of olefins as well as those of saturated hydrocarbons as causes of the smog nuisance. Although with the rapid turnover used in the fumigation chamber the irritating effects of the oxidation products of saturated hydrocarbons could not be established, these reactions should not be excluded from consideration, especially when branched hydrocarbons are exposed for several hours, as is the case in the free atmosphere. These oxidations have been shown to occur with nitrogen oxides, sunlight, and hydrocarbons, such as 2,2,4-trimethylpentane and 3-methylheptane.

Included in the general picture is the oxidation of sulfur dioxide to sulfur trioxide as a contributor to the decrease in visibility. This oxidation is known to be catalyzed in the presence of nitrogen oxides, which are released at the same time in combustion processes. In plant as well as in rubber cracking experiments it was found that sulfur dioxide opposes the action of the oxidant, and its role in a possible formation of atomic oxygen through photochemical oxidation appears unlikely.

The investigations on crop damage, eye irritation, and finally rubber cracking, all lead to the conclusion that the major source of the typical smog nuisance is to be found in the release to the atmosphere of hydrocarbons and nitrogen oxides. The strong oxidizing action in the smog air, caused by the action of nitrogen oxides and sunlight, converts hydrocarbons into products of peroxide nature and to aldehydes and acids. In the course of this photochemical oxidation ozone is formed, which contributes to the oxidation of additional quantities of organic material and which is responsible for the increase of rubber cracking during smog periods. Peroxides, as well as ozone, are irritating to plant and animal, and therefore the substances responsible for their formation, the nitrogen oxides, hydrocarbons and their derivatives, should be considered as potentially toxic materials. In the atmospheric oxidation of hydrocarbons aerosols are formed, contributing to an already present decrease in visibility caused by other sources. Each one of these reactions has been duplicated in the laboratory, and the analytical data on material collected from smog air are in harmony with these views.

These studies clearly demonstrate that pollutants from the moment of their release are subjected to the action of natural components of the air as well as that of other pollutants. Photochemical and other reactions change normally harmless compounds into objectionable ones. On the other hand, substances irritating when released may soon be converted into harmless ones. A proper evaluation of the contribution of air pollutants to the smog nuisance must include not only the time and place of their emission, but also their fate in the air.

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