

If a change from oxygen to air is also involved, the effect of the changes in oxygen concentration must also be taken into account.

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Ozone Formation in Photochemical Oxidation of Organic Substances

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SMOG periods in the Los Angeles area are chemically characterized by a pronounced oxidizing effect, in the order of 0.6 p.p.m. (volume per volume), calculated as hydrogen peroxide, and usually measured by the liberation of iodine from neutral buffered potassium iodide solution.

The oxidizing action of smog can also be measured by the decolorization of dyes such as indigo sulfonic acid or crystal violet. On the other hand, leuco dyes are readily oxidized to the corresponding colored compounds. A convenient smog indicator is colorless phenolphthalein which is oxidized to phenolphthalein, giving a red color in alkaline solution. The intensity of the red color is a direct measure of the smog concentration. The rapid oxidation of cysteine and glutathione during smog periods is of interest since the oxidation of sulfhydryl groups has been correlated with lachrymatory action (2).

It has been shown that this oxidizing effect of smog is due to the combined action of nitrogen oxides, peroxides, and ozone, counteracted by the reducing action of sulfur dioxide, which is present in concentrations of 0.1 to 0.2 p.p.m.

The presence of peroxides is explained by the photochemical oxidation of large quantities of hydrocarbons released into the air. In this reaction, nitrogen oxides play the role of catalysts (4, 6). The more puzzling fraction of the oxidant is the ozone, which reaches concentrations as high as 0.3 p.p.m. as determined by rubber cracking experiments. The development of a quantitative rubber cracking test for ozone made it possible to follow this phenomenon during smog periods and to express the degree of cracking in concentrations of ozone which would give, under the same experimental conditions, the same, typical cracking (1). The time necessary for initial cracking of rubber during a smog

period can be as short as 4 minutes, whereas on normal days this takes from 45 to 60 minutes. These cracking times correspond, respectively, to 0.3 and 0.02 p.p.m. of ozone.

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 have been confirmed by the authors of this paper 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.

OZONE FORMATION WITH NITROGEN OXIDES

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. When nitrogen oxides in concentrations of 0.4 p.p.m. in air were exposed for a few hours to sunlight, bent rubber pieces often showed typical ozone cracking. But when air purified by passing through activated carbon filters, or when pure oxygen was used in addition to nitrogen oxides, no cracking of rubber took place upon exposure to sunlight. The laboratory air contained, therefore, enough impurities to give rubber cracking when nitrogen oxides were present.

Rapid rubber cracking, comparable to that observed during smog periods, was repeatedly observed during plant fumigation experiments, when hydrocarbons, nitrogen oxides, and sunlight

TABLE I. OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH 3-METHYLHEPTANE AND NITROGEN DIOXIDE IN SUNLIGHT

(Exposure time 3 hours; 2-liter reaction flasks)		
3-Methylheptane, P.P.M.	Nitrogen Dioxide, P.P.M.	Average Rate of Ozone Formation, P.P.M./ Hour
70	0.4	None
3	0.4	0.4
1	0.4	1.0
0.1	0.4	1.3
1	0.1	0.2
1	0.02	None
1.4	None	None

TABLE II. OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH ORGANIC ACIDS, NITROGEN OXIDES, AND SUNLIGHT

Test Acid	Concn., P.P.M. (V/V)	Nitrogen Oxides, P.P.M. (V/V)	Flask Volume, L.	Exposure Time, Min.	Average Rate of Ozone Formation, P.P.M./ Hour
Formic	1	0.4	2	120	0
Acetic	1	0.4	2	120	0.1
Propionic	1	0.4	2	120	0.3
Butyric	1	0.4	2	120	0.5
Valeric	1	0.4	2	120	1.0
Caproic	1	0.4	2	120	1.0
Heptylic	1	0.4	2	120	1.0
Caprylic	1	0.4	2	120	0.8
Diethyl acetic	1	0.4	2	180	1.0
Diethyl acetic	0.1	0.4	12	5	0.8
Diethyl acetic	0.1	0.4	12	6	1.3
Diethyl acetic	0.1	0.4	12	20	1.2
Methyl ethyl acetic	1	0.4	2	240	0.6
Pyruvic ^a	1	0.4	5	210	0.3

^a At higher concentrations, rubber cracking observed in absence of nitrogen oxides.

were used, and this led to the suspicion that ozone might be formed in the photochemical oxidation of organic substances.

To study this reaction further, experiments were conducted in borosilicate glass flasks containing air with varying concentrations of organic substances and nitrogen oxides. The air was filtered through activated charcoal filters. Since these experiments simulated atmospheric conditions, no attempt was made to remove the water from the air, and later experiments showed that traces of water were essential for the reaction. Bent strips of rubber were suspended in the flasks before exposing them to sunlight. The rubber cracking obtained was compared with that given by known concentrations of ozone.

It was postulated that peroxides play a role in the formation of ozone, and branched, saturated hydrocarbons were selected as test materials since these substances readily yield peroxides on photochemical oxidation with nitrogen dioxide. When the reaction is carried out in the presence of rubber, no isolation of the peroxides is necessary, thereby avoiding the destruction of the most active primary oxidation products. Since the success of the experiment depends on a preferential oxidation of the rubber, a saturated hydrocarbon was chosen, rather than an olefin.

Using a concentration of 0.1 p.p.m. of 3-methylheptane and 0.4 p.p.m. of nitrogen dioxide in air, in a 2-liter flask, pronounced rubber cracking was observed in 1 hour, while in parallel experiments using either one alone at the same concentration, no cracking was seen in 5 hours. Table I contains the data obtained with different concentrations of 3-methylheptane and nitrogen oxides. Photochemical formation of the rubber cracking material takes place only at low concentrations of hydrocarbon, and a large excess of hydrocarbon completely inhibits the rubber cracking. Quenching action on photochemical processes has been observed frequently in other cases.

When the flasks filled with air containing 3-methylheptane and nitrogen dioxide were exposed to sunlight for several hours and

bent rubber strips were subsequently introduced, heavy cracking was observed in the absence of light. The rubber cracking material is therefore stable. When the contents of the flask were passed through a ferric ferriyanide solution, the solution turned blue because of the presence of peroxides and nitrogen oxides. The rubber cracking material, however, was not absorbed. After passing through the solution, its presence can be demonstrated by rubber cracking and iodine release from potassium iodide solutions. This behavior indicates that the rubber cracking material is ozone, and its presence was confirmed by isolation from the reaction mixture by condensation.

When the contents of a 12-liter flask of irradiated nitrogen dioxide (0.4 p.p.m.) plus 3-methylheptane (2 p.p.m.) in air were slowly drawn through a series of Shepherd absorption traps held, respectively, at -20° , -80° , and -180° C., the first two traps contained all the nitrogen oxides and peroxides. The rubber cracking material collected in the -180° C. trap. This behavior on fractional condensation, the liberation of iodine from neutral potassium iodide solution, decolorization of crystal violet and indigo sulfonic acid solutions, and the typical ozone smell of the condensate from the -180° C. trap established the presence of ozone.

The strong rubber cracking observed with 3-methylheptane and nitrogen dioxide in air seems to be a rather general phenomenon in the photochemical oxidation of organic substances, and the authors have observed this action with other hydrocarbons, as well as with their oxidation products—acids, aldehydes, and alcohols.

In a series of straight-chain organic acids, ranging from formic to pelargonic acid, the optimum effect after photochemical oxidation with nitrogen dioxide in air was found with the acids containing five to eight carbon atoms (Table II). Formic acid gave no rubber cracking. Branched-chain organic acids also produced ozone in these experiments. For example, with diethylacetic acid at 0.1 p.p.m. in air and 0.4 p.p.m. nitrogen dioxide, in a 12-liter flask, definite rubber cracking was obtained in a 5-minute exposure to sunlight. The ozone formed was isolated by fractional condensation and identified as described in the case of 3-methylheptane.

TABLE III. OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH ORGANIC COMPOUNDS, NITROGEN OXIDES, AND SUNLIGHT

Test Material	Concn., P.P.M. (V/V)	Nitrogen Oxides, P.P.M. (V/V)	Flask Volume, L.	Exposure Time, Min.	Average Rate of Ozone Formation, P.P.M./ Hour
Isobutane	1	0.4	2	180	0.2
n-4-Nonene	0.1	0.4	2	180	0.2
Mesitylene	1	0.4	2	240	0.9
Ketene	1	0.4	2	120	0.9
Diethyl carbinol	1	0.4	2	240	0.9
Methyl propyl carbinol	1	0.4	2	180	0.5
n-Butyraldehyde	0.1	0.4	2	210	0.4
n-Butyraldehyde	1	0.4	2	180	0.5

In Table III the ozone formation in the photochemical oxidation of a miscellaneous group of substances with nitrogen oxides is given. No cracking was observed in the absence of nitrogen oxides. No cracking was noticed in the presence of 0.4 p.p.m. of nitrogen oxides with acetone, acetyl acetone, formaldehyde, carbon monoxide, isopropyl alcohol, methane, ethane, or propane.

In Table IV are listed oxidation experiments with different concentrations of nitrogen dioxide in air, while the concentration of the organic material, caprylic acid, was kept constant at 1 p.p.m. Optimum effect is noticed at concentrations which have been measured during severe smog.

TABLE IV. OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH CAPRYLIC ACID AND NITROGEN DIOXIDE IN AIR WITH SUNLIGHT

(Exposure time 1 hour; 2-liter reaction flasks)

Caprylic Acid, P.P.M. (V/V)	Nitrogen Dioxide, P.P.M. (V/V)	Rate of Ozone Formation, P.P.M./Hour
1	20	0.4
1	5	0.6
1	2	0.7
1	0.4	0.8
1	0.1	0.6
None	20	None
None	0.4	None

In Table V are listed rubber cracking data obtained with 10° C. fractions of ethyl gasoline as source of hydrocarbon. The concentration of the gasoline fractions in air was 1 p.p.m. and the nitrogen oxide concentration was 0.4 p.p.m. In concentration of 0.1 p.p.m., when oxidized with 0.4 p.p.m. nitrogen dioxide in sunlight for 1 hour, the 70° to 80° C. fraction gave rubber cracking corresponding to 0.2 p.p.m. ozone.

The ozone formation with gasoline fractions is attributed to their content of branched, unsaturated hydrocarbons and olefins. Olefins which, upon oxidation with nitrogen dioxide and sunlight, yield aldehydes and acids of the proper chain length can be expected to contribute to the ozone formation. This was confirmed by the photochemical oxidation with 0.4 p.p.m. nitrogen dioxide of 0.1 p.p.m. *n*-4-nonene, whereby 1.4 p.p.m. of ozone were formed in 3 hours. The oxidation of *n*-4-nonene results in the formation of *n*-butyric and *n*-valeric acids and the corresponding aldehydes, all of which are active in ozone production.

TABLE V. OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH GASOLINE FRACTIONS (1 P.P.M.) AND NITROGEN DIOXIDE (0.4 P.P.M.) IN AIR AND SUNLIGHT

(Exposure time 3 hours; 2-liter reaction flasks)

Gasoline Fraction, B.P., ° C.	Rate of Ozone Formation, P.P.M./Hour
0-40	0.2
40-50	None
50-60	None
60-70	0.6
70-80	0.9
80-90	0.4
90-100	0.3
100-110	0.4
110-120	0.4
120-130	0.4
130-140	0.4
140-150	None
150-160	None
160-170	0.2
170-180	0.2
Blank, NO ₂ only	None

A comparison of the ozone concentrations obtained in many of the photochemical oxidations with the concentrations of nitrogen dioxide and organic substances used shows that the amount of ozone formed is several times greater than could be theoretically developed from a stoichiometric reaction of the hydrocarbon and nitrogen dioxide. It was therefore concluded that ozone is formed in a chain reaction. The photochemical dissociation of nitrogen dioxide with sunlight provides a continuous source of atomic oxygen for this reaction, since nitrogen dioxide is regenerated through oxidation of nitric oxide by molecular oxygen. The formation of ozone is therefore dependent on the presence of oxygen. It has been shown that replacement of air with nitrogen completely suppresses the rubber cracking. It is postulated that in the chain reaction leading to ozone formation, peroxide radicals are formed which react with molecular oxygen to form ozone.

After the peroxide radical has released one of its oxygen atoms, it may be reoxidized and again react with molecular oxygen.

Intermediate steps in the reaction with oxygen might consist in the formation of HO₂ radicals, which subsequently react with a peroxide radical to give ozone. The fact that water must be present in these reactions lends support to the postulation of this intermediate step.

Ozone formation in the photochemical oxidation of organic material and its explanation parallels that of the ozone formation in the oxidation of inorganic substances such as phosphorus. Fischbeck and Eich, in 1938, in a study of the ozone formation with phosphorus and oxygen, gave evidence that this formation takes place through a chain mechanism involving the formation of phosphoric oxides and peroxides (3). In the case described in this paper, the alkyl radicals formed might serve in a similar way as oxygen acceptors.

OZONE FROM DIKETONES AND ALKYL NITRITES

To test the peroxide radical chain hypothesis in the formation of ozone, the photochemical oxidation of biacetyl was studied, since it is known that biacetyl, under the influence of light, easily forms free radicals. In this experiment, nitrogen dioxide is not necessary for the transfer of light energy, since biacetyl absorbs light in the visible range of the spectrum. Biacetyl, in concentration of 2000 p.p.m. in air in a 2-liter borosilicate glass flask, gave rapid rubber cracking. The contents of the flask were drawn through Shepherd traps held at -20°, -80°, and -180° C. After warming the -180° trap to -100° C. while passing nitrogen through, the gas released decolorized crystal violet and indigo sulfonic acid solutions, liberated iodine from neutral buffered potassium iodide solution, did not affect ferric ferri-cyanide solution, and had the typical ozone smell. When passed over a rubber test strip, rubber cracking was observed within seconds. Traces of water are necessary in the formation of ozone, since thoroughly dried air and biacetyl failed to give rubber cracking.

In an experiment using six 22-liter flasks in series, each containing 2000 p.p.m. biacetyl, the ozone formed was isolated by fractional condensation and its identity confirmed by R. Badger through infrared spectroscopic analysis.

TABLE VI. PHOTOCHEMICAL OZONE FORMATION FROM BIACETYL

Exposure Time, Min.	Ozone Formed, P.P.M. (V/V)	
	Biacetyl, 2000 p.p.m.	Biacetyl, 20,000 p.p.m.
2	3	..
4	9	..
8	14	..
16	19	..
20	22	..
30	30	64
40	28	..
60	28	83
120	..	60
150	24	..
240	2	31
480	1	0

The lowest concentration of biacetyl at which cracking of rubber could be observed without addition of nitrogen oxides was 40 p.p.m. This concentration is considerably higher than that of the hydrocarbons used in the photochemical oxidation with nitrogen dioxide. The main reason for this is probably the irreversible decomposition of biacetyl in light to products such as acetyl peroxide, peracetic acid, acetic acid, and formic acid. These do not form ozone under the influence of sunlight.

In separate 2-liter borosilicate glass flasks, samples of biacetyl in air were exposed to bright sunlight for varying periods of time.

The contents of the flasks were then passed through a series of three Shepherd traps held at -100°C ., and then through a bubbler containing neutral buffered potassium iodide solution. The iodine released was titrated with 0.001 *N* sodium thiosulfate solution, and the ozone concentration calculated. The entire oxidizing effect was due to ozone, since peroxides and other oxidants were effectively retained in the traps. Table VI shows that after 30 minutes the ozone concentration had reached a maximum concentration of 30 p.p.m.

When the biacetyl concentration is increased by a factor of 10 the maximum obtainable ozone concentration is increased by a factor of only 2.5. The observed ozone formation is therefore not directly proportional to the biacetyl concentration, but depends on side reactions such as the reaction of the ozone formed with oxidation products of biacetyl and with biacetyl itself.

Bibutyryl, also a 1,2-diketone, gives rubber cracking, and therefore ozone, when exposed to sunlight in the absence of nitrogen oxides. Ozone formation has been observed using the α -keto acid, pyruvic acid. The amount of ozone formed is considerably less than in the case of biacetyl, but can be readily demonstrated by the cracking of a bent piece of rubber suspended during or after irradiation in a flask containing pyruvic acid. As in the case of biacetyl, ozone formation can be observed with a concentration of 1 p.p.m. when 0.4 p.p.m. nitrogen dioxide is present. The expectation of ozone formation by compounds which upon oxidation would give rise to pyruvic acid was verified by exposing mesitylene in air with 0.4 p.p.m. of nitrogen dioxide to sunlight (Table III).

Rubber cracking without the addition of nitrogen oxide is also observed when butyl nitrite in a concentration of 0.1 p.p.m. is exposed to sunlight. It is known that in the absence of oxygen, alkyl radicals and nitrogen oxides are formed by the decomposition of butyl nitrite. The expectation that, in the presence of oxygen, ozone would be formed was confirmed by the rapid rubber cracking observed.

ECONOMIC AND HEALTH ASPECTS

In the photochemical oxidation with nitrogen dioxide and organic substances—hydrocarbons and their oxidation products—ozone is formed in concentrations as high as several parts per million. The concentration of the organic materials used in these experiments, as well as that of nitrogen dioxide, is of the same order as those found in the Los Angeles atmosphere during smog periods.

The Los Angeles County Air Pollution Control District found that in the processing, handling, and use of hydrocarbons, large quantities of hydrocarbons, in the order of 2000 tons, are emitted daily to the air, while simultaneously 250 tons of nitrogen oxides are released from combustion processes. Analyses of the smog air have shown the presence of 1 to 2 p.p.m. of hydrocarbons and 0.4 p.p.m. of nitrogen oxides (6).

The abnormally high ozone content of smog air and consequent severe rubber cracking during such a period is, therefore, readily accounted for by the ozone formed in oxidation reactions.

Cracked gasoline consists mainly of branched saturated hydrocarbons and olefins which are rapidly oxidized by nitrogen oxides in the presence of sunlight. In this oxidation irritating peroxides, acids, aldehydes, and ozone are formed (5). The organic acids and aldehydes of proper chain length produce further quantities of ozone with nitrogen dioxide and sunlight.

The combustion of the organic material in the air is therefore a gradual one. During the shortening of the chain, many of the intermediates may function in turn as ozone producers. Peroxide radicals, appearing as intermediates in this degradation, are postulated to produce ozone through their reaction with molecular oxygen.

Under the meteorological and geographical conditions existing in the Los Angeles area, the release of hydrocarbons and nitrogen

dioxide in this area could lead to ozone concentrations of several parts per million. Fortunately, its accumulation is limited by the following factors:

- Action of reducing compounds such as sulfur dioxide
- Decomposition by light
- Gradual degradation of the organic compounds to carbon dioxide and the formation of nonvolatile polymerization products
- Addition reactions with aromatic compounds and unsaturated hydrocarbons such as acetylene and ethylene which do not form ozone in the photochemical oxidation with nitrogen dioxide
- Oxidation of nitrogen oxides to nitric acid
- Removal of nitrogen dioxide by the formation of nonvolatile nitro compounds

These reactions are responsible for the rapid decrease in ozone concentration toward evening when the photochemical regeneration of ozone has come to an end. During smog periods the formation of ozone outweighs its destruction, and ozone concentrations of 0.2 to 0.3 p.p.m. have repeatedly been recorded. These concentrations are several times greater than the maximum level of 0.1 p.p.m. recommended for safe working conditions by the American Medical Association Council on Physical Therapy.

The abnormally high ozone concentrations found in the Los Angeles area during a smog period, formed, as shown, by the photochemical oxidation of hydrocarbons by sunlight in the presence of nitrogen oxides, present not only a health hazard but also a problem of considerable economic importance (4).

In view of the photochemical formation of ozone at ground level, the rubber industry, in planning its storage facilities, must consider not only the ozone already present in the air but also the potential sources of ozone such as the simultaneous presence of hydrocarbons, their oxidation products, and nitrogen oxides. It has been found that the resultant ozone can be effectively removed through the use of activated carbon filters. When storage in the open air is necessary, the contamination of the area with gasoline vapors and nitrogen dioxide producing combustions, such as take place in the automobile, should be avoided.

SUMMARY

The formation of ozone through photochemical oxidation of alcohols, aldehydes, ketones, acids, and hydrocarbons such as are present in gasoline in the presence of small quantities of nitrogen oxides has been demonstrated. Ozone production without the addition of nitrogen oxides has been observed in the photochemical oxidation of biacetyl, bibutyryl, pyruvic acid, and butyl nitrite. The ozone produced in these reactions was identified by chemical and physical methods. The ozone formation is attributed to a peroxide radical chain reaction.

The release of large quantities of hydrocarbons to the air and the simultaneous presence of nitrogen oxides from combustion processes explains the relatively high ozone content, and consequent severe rubber cracking, in the Los Angeles area. These findings should be considered in planning rubber storage facilities.

In view of the irritating properties of the products formed by this photochemical oxidation, both hydrocarbons and nitrogen oxides should be considered as potential irritants when they occur simultaneously in the air at low concentrations.

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