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Reactions of ozone with unsaturated fatty acids

By Gaku Izumi

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REVIEW

Reactions of Ozone with Unsaturated Fatty Acids

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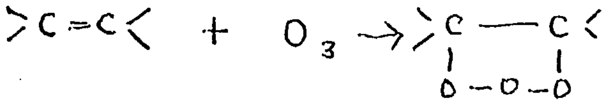
INTRODUCTION

During the last few years there have been extensive studies regarding the formation of mono- and di-carboxylic acids, aldehydes, amines, and omega-amino acids from unsaturated fatty acids and the identification of the structures of unsaturated fatty acids using ozenolysis techniques. This extensive study has been made possible through the development of ozonizers both of an efficient industrial size and of a convenient laboratory size for research purposes. The first paper about the reactions of ozone with organic compounds was published by Schönbein in 1855[2]. In 1873 Houzeau[3] succeeded in separating an ozonide which was obtained by the reaction of ozone with benzene. During 1901-1916, Harries[4], [5] studied systematically the mechanism of the decomposition reaction of ozonides and established the fundamentals for future study in the field. Standinger[6] proposed a new theory for the mechanism of the ozonolysis in 1925. After the successive studies by Rieche[7] in 1931, by F.G. Fisher[8] in 1932, by Pummer[9] in 1937 and by Briner et. al.[10] in 1938 on the mechanism of the reaction, Criegee et al.[1] proposed a new hypothesis for the mechanism. The many studies by workers in the early days before the presentation of the Criegee's hypothesis regarding the reaction of ozone with general organic compounds have been reviewed by Long[11] in 1940 and by Bailey[12] in 1958. In this paper, the reaction mechanism of ozonolysis and the recent studies of ozonolysis of unsaturated fatty acids are reviewed chronologically.

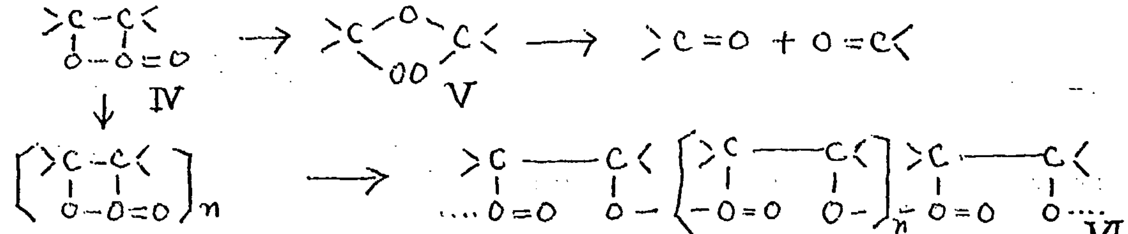
2. Reaction Mechanism of Ozonolysis

In 1910, Harries[13] proposed the following mechanism; ozone (II) reacts with the ethylene bond (I) and produces an addition product. (III).



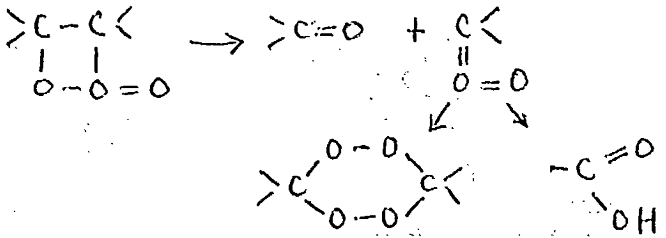
I II III

However, Fisher[8)] in 1932 and Pummer[9)] in 1937 could not confirm the formation of glycol which was expected as a reduction product of the ozonide using a number of different mild reduction methods. In 1925, Staudinger[6)] proposed that in ozonization an ozonide monomer (IV) instead of (III) will be produced and then be transferred to a stable iso-ozonide (V) by rearrangement, or a high molecular weight compound (VI) will be produced by polymerization.

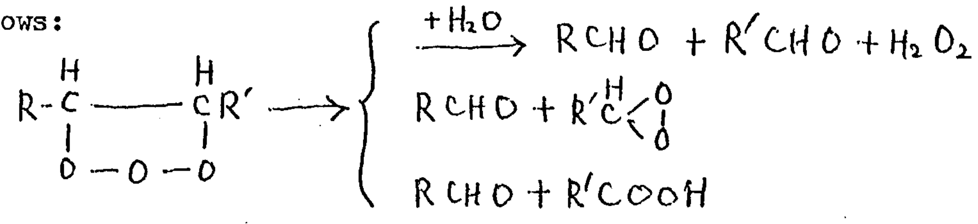


IV V VI

With this theory, it was explained that glycol was not obtainable as a reduction product but aldehyde, ketone or corresponding alcohol would be obtained instead. This theory predicted that the polarity of the solvent would greatly influence the reaction. For example, there was less possibility for ozonide to associate in acetic acid because of its high polarity and only ozonide monomer would be obtained. On the other hand, polymer would be obtained in carbon tetrachloride, because the association takes place easily in this non-polar solvent. He also explained that there was a possibility for an ozonide monomer to decompose immediately to give ketone peroxide, ketone, or the corresponding acid.



The decomposition mechanisms of (III) suggested by Harries[13)] in 1910 are as follows:



The following are the mechanisms suggested by Rieche7) in 1931, which are based on his many experimental results.

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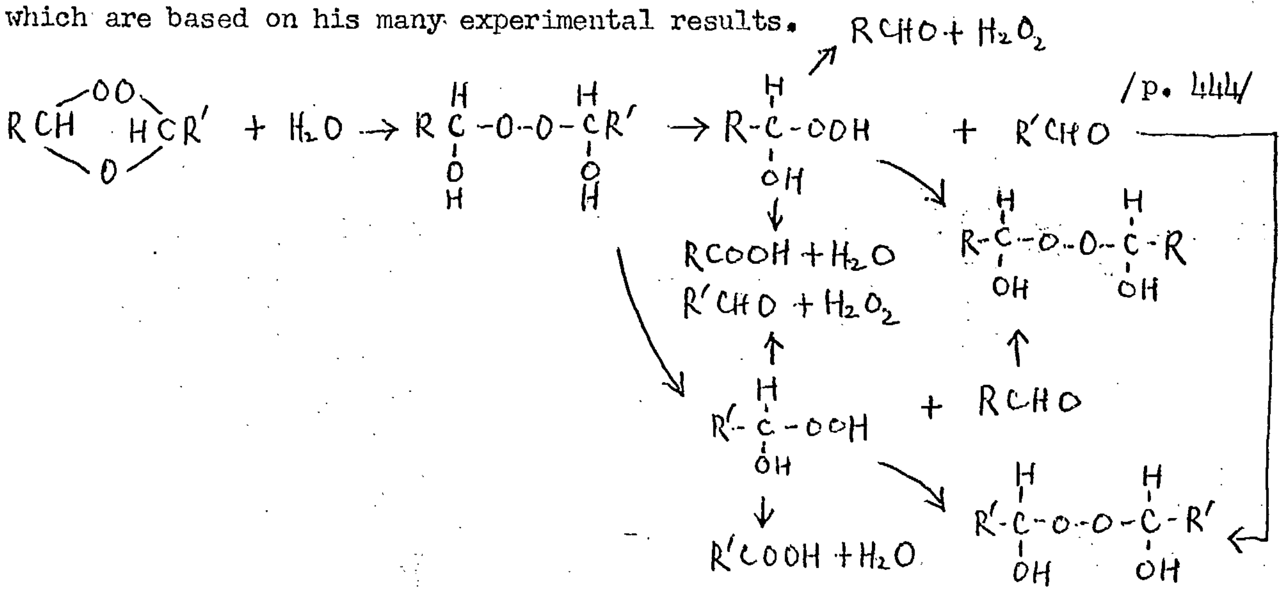
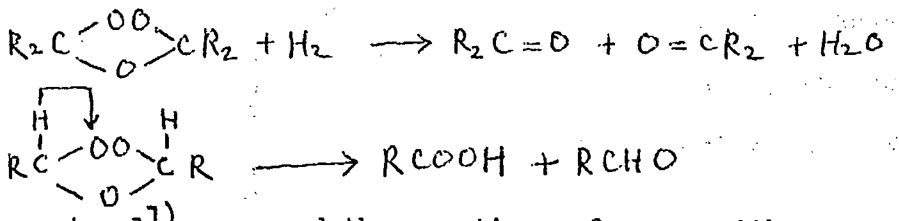
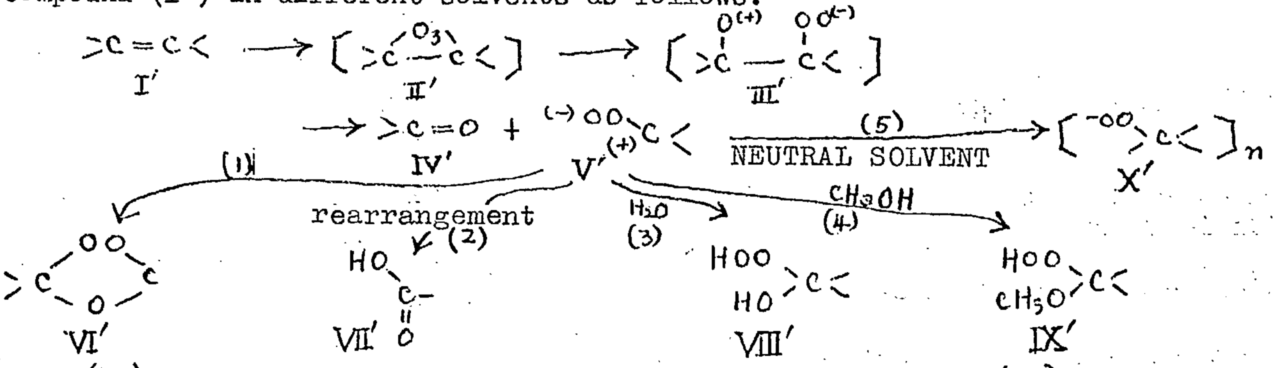


Fisher8) proposed a new method of ozonolysis with a contact hydrogenation method in 1932. In this reaction, acid was formed by "acid rearrangement", and the "acid rearrangement" should be accelerated at higher temperatures. The reactions suggested are as follows.



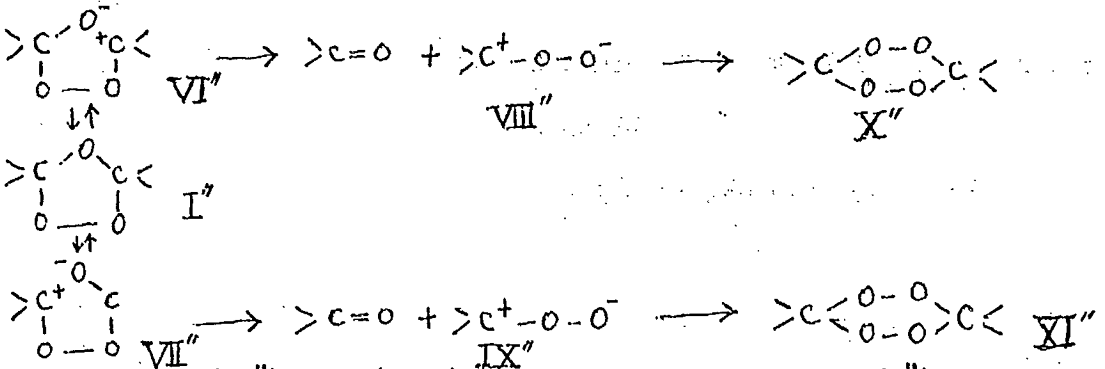
Criegee et. al1) proposed the reactions of ozone with an unsaturated compound (I') in different solvents as follows:



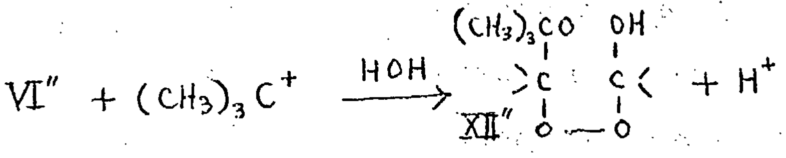
(I') will react with ozone and produce carbonyl compound(IV') and amphoteric ion (V'), via intermediate products (II') and (III') and;

1) (IV') will react with (V') and give an ozonide monomer (VI').
2) (V') will be rearranged to acid (VII').
3) (V') will react with H_2O which is used as a solvent and give an oxyhydro peroxide (VIII').
4) (V') will react with CH_3OH and give methyl hydro peroxide (IX')
5) (V') will give a polymer (X') in a neutral solvent.

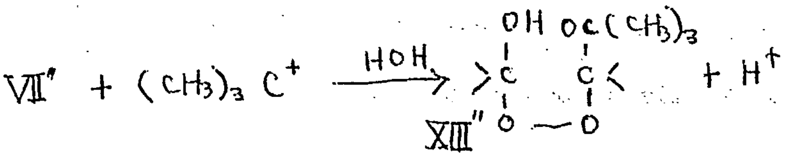
Milas et. al.[14] proposed a different idea in 1955 as follows.



Amphoteric ions (VI") and (VII") are in equilibrium with (I"). If there is no reagent to participate with the reaction, (VI") or (VII") will decompose to give ketone or aldehyde and amphoteric ions (VIII" and IX"). The resulting (VIII") and (IX") will change to alkylidine peroxides (X" and XI"), which are very explosive. When the ozonization is carried out in the presence of a carbonium ion, (I"), (X") and (XI") are not produced, and peroxide (XII" and XIII") will be produced instead. Examples are as follows:



$$VI'' + (CH_3)_3C^+ \xrightarrow{HOH} XII'' + H^+$$



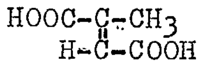
$$VII'' + (CH_3)_3C^+ \xrightarrow{HOH} XIII'' + H^+$$

3. Oxidation reaction of Ozone and rate of Ozonization

As mentioned in section 2 above, ozone has a preference for the ethylene bond in the reaction with an unsaturated compound. However, ozone in the ozonized oxygen (a mixture of ozone and oxygen) has an effect as an oxydation catalyst on a saturated hydrocarbon bond[15].

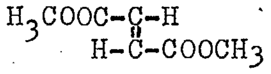
This catalytic effect is stronger in lower concentration of ozone. From the observation of infrared spectra16),17) and from the study of hydrogenolysis products of ozonides, the author assumed that ozonides formed in glacial acetic acid from oleic acid and methyl oleate consisted of acetoxyhydroperoxides which were obtained by the reaction of acetic acid with the amphoteric ions as suggested by Criegee et. al.1) and of hydroperoxide which was a product obtained by self-oxidation. Under normal conditions, a carboxyl group reacts with ozone only a little20), but under the exposure of ultra-violet light peracetic acid will be obtained from acetic acid21).

Harries22) and Brus et al.23) studied the rate of ozonation. Noller et. al.24) studied the relationship between the molecular structures of unsaturated compounds and the rate of ozonation using the Brus' method: 0.05 ml of sample was dissolved in 125 ml of glacial acetic acid, ozonized air containing about 5 wt % of ozone was passed into the solution at a rate of 1.25 /min. and the amount of unabsorbed ozone was measured every five minutes and finally the amount of ozine which reacted was calculated. From many results, he found that for methyl oleate, oleic acid and elaidic acid, ozone was absorbed stoichiometrically. When there is a double bond conjugated with a carbonyl group such as in crotonic acid $CH_3CH=CHCOOH$, /P.445/ cinnamic acid $C_6H_5CH=CHCOOH$, or itaconic acid $CH_2=C(COOH)CH_2COOH$, the rate of absorption of ozone was slowed down markedly. The retarding effect of the carbonyl group is, however, not so noticeable when the carbonyl group is not conjugated with a double bond and is separated by O, such as in vinyl acetate $CH_2=CHOCOCH_3$. The retarding effect is more noticeable in itaconic acid, which has two carbonyl groups; one is conjugated with the double bond, and the other is not. When there are three conjugated double bonds such as eleostearic acid, the first mole of ozone will be absorbed rapidly and then the rate of absorption slows down. In the case of sorbic acid $CH_3CH=CHCH=CHCOOH$ which has the double bonds alpha and beta to the carbonyl, the rate of ozone absorption after the first mole is absorbed, is slower than for that of eleostearic acid. In the case of cis- and trans-isomers, there is no marked difference between oleic acid and elaidic acid in the rate of absorption of ozone. However, when there is a carbonyl group conjugated with a double bond, the rate of ozone absorption is much faster in the trans-form such as in mesaconic acid



$$\begin{array}{l}\mathrm{HOOC{-}C{-}CH_3}\\ \quad\ \mathrm{H{-}\overset{\|}{C}{-}COOH}\end{array}$$

and methyl fumarate

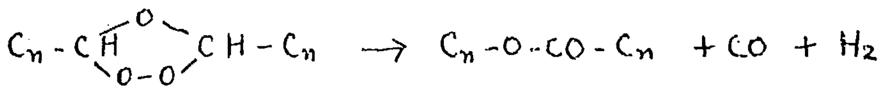


$$\begin{array}{l}\mathrm{H_3COOC{-}C{-}H}\\ \qquad\quad\mathrm{H{-}\overset{\|}{C}{-}COOCH_3}\end{array}$$

than in the cis-form such as in citraconic acid, maleic acid and methyl maleate. The retarding effect was greater when two conjugated carbonyl groups were present than when only one was present.

4. By-products by Ozonolysis

In most cases, carbonyl compounds and acids will be produced by ozonolysis. However, Ackman et. al.[25)] obtained octanol and octyl formate when the ozinide obtained from oleic acid in methanol was decomposed by adding formic acid and hydrogen peroxide. They assumed that the reaction would be shown in the following form as suggested by Pasero et. al.[59)]



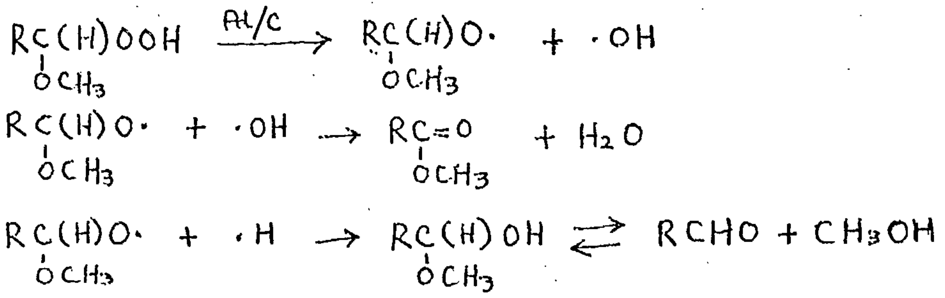
Thus the monooctyl azelate produced is expected to hydrolyse or transesterify to give both octanol and octyl formate in the presence of fomic acid and water.

5. Ozonolysis of Oleic Acid Family

In 1906, Harries et. al.[26)] treated 16g of ozonide obtained in glacial acetic acid with water on a water bath for 30 min. and decomposed to give 2.8g of pelargon aldehyde, 5.0g of pelargonic acid, 3.5g of mixture of azelaic acids and 4.2g of distillation residue; 15.5g as total. In 1910, Franck[27)] treated 12g of ozonide with a double amount of glacial acetic acid for 30 min on a water bath and obtained 3.4g of azelaic acid (including peroxide), 2.5g of azelaic acid half aldehyde, 2.9g of pelargonic acid and 1.8g of pelargon aldehyde (including peroxide); 10.6g as total.

In 1926, Noller et al.28) treated oleic acid, undecylenic acid and the methyl ester of erucic acid with ozone in glacial acetic acid to form their ozonides, then ethyl ether, zinc powder and water were added and the ozonide was decomposed by heating. With this treatment, pelargon aldehyde, eta-aldehyde octanoic acid, theta-aldehyde nonanoic acid and methyl ester of lambda-aldehyde dodecanoic acid were obtained with more than 55% of the theoretical recovery. In 1932, Fisher et. al.8) succeeded in obtaining aldehydes with a 50-70% recovery from oleic acid ozonide in methanol by contact reduction using a palladium-calcium carbonate catalyst under high pressure. In 1935, Obata29) obtained 40% of pelargonaldehyde and 33% of azelaic acid half aldehyde from oleic acid ozonide obtained in chloroform, by decomposition with heating in the presence of ethyl acetate, acetic acid (not glacial) and zinc powder under a current of carbon dioxide. In 1942, Rieche et. al.30) decomposed oleic acid ozonide with iron and acetic acid and obtained oxynonyl-peroxide and dioxynonyl-peroxide dicarbonic acid. In 1956, the author18) studied the reaction of ozone with methyl oleate and oleic acid in glacial acetic acid and the decomposition reaction of the reaction products. In 1960, Pryde et. al.31) studied the effect of solvents when ozone reacts with methyl oleate and the reduction decomposition of the ozonide in the presence of acetic acid-zinc powder or palladium-active carbon-hydrogen. In this study they found that in polar solvents such as methanol or acetic acid carbonyl compounds were obtained with an 87% recovery (before separation, it was 90-92% by the hydroxylamine method) whereas in non polar solvents such as ethyl acetate or heptane, the recovery was very poor and the products included large amounts of impurities. In 1961, Ackman et. al.25) obtained azelaic acid with more than 95% of recovery from an ozonide obtained in methanol from oleic acid by oxidation decomposition in the presence of hydrogen peroxide in formic acid.

In 1962, Pryde et. al.32) found that a large amount of dimethylester of azelaic acid was obtained as a side product when a partially ozonized compound which was obtained from methyl oleate in methanol was reduced using a palladium-carbon catalyst. However, when the hydrogenation of the ozonide was carried out in the presence of pyridine, the amount of the side product and the effectiveness of the catalyst for the olefinic compounds were decreased. Thus, the yield and the purity of aldehydeester were increased and it became possible to recover the unreacted methyl oleate. The reactions suggested are as follows:



$$R\underset{\substack{|\\ OCH_3}}{C}(H)OOH \xrightarrow{Pt/C} R\underset{\substack{|\\ OCH_3}}{C}(H)O\cdot + \cdot OH$$

$$R\underset{\substack{|\\ OCH_3}}{C}(H)O\cdot + \cdot OH \longrightarrow R\underset{\substack{|\\ OCH_3}}{C}{=}O + H_2O$$

$$R\underset{\substack{|\\ OCH_3}}{C}(H)O\cdot + \cdot H \longrightarrow R\underset{\substack{|\\ OCH_3}}{C}(H)OH \rightleftarrows RCHO + CH_3OH$$

$$H\cdot + \cdot OH \longrightarrow H_2O$$

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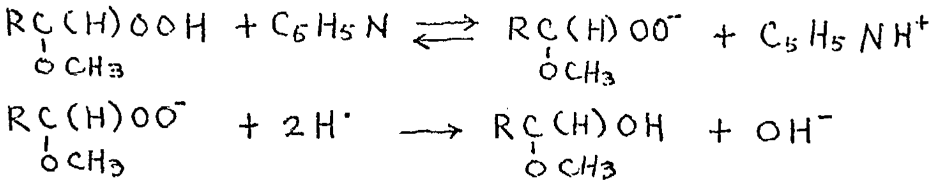
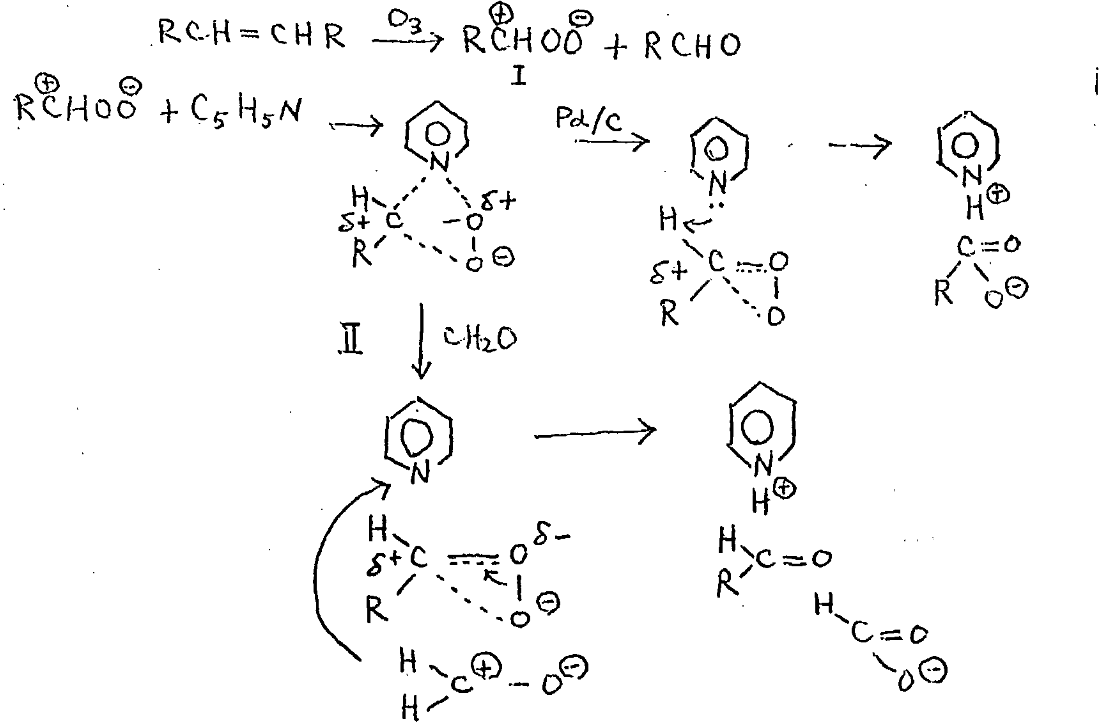
When pyridine is added, hydroperoxide amion is presumed to become a form of hemiacetal, so the formation of dimethylester of azelaic acid decreases and there is no increase in the yield of aldehyde.



$$R\underset{\substack{|\\ OCH_3}}{C}(H)OOH + C_6H_5N \rightleftarrows R\underset{\substack{|\\ OCH_3}}{C}(H)OO^- + C_5H_5NH^+$$

$$R\underset{\substack{|\\ OCH_3}}{C}(H)OO^- + 2H^\cdot \longrightarrow R\underset{\substack{|\\ OCH_3}}{C}(H)OH + OH^-$$

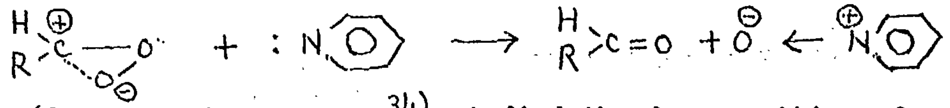
When there is no reactive solvent, such as methanol, relatively stable complex II will be obtained and if there is a suitable catalyst, II will form a pyridine salt getting a proton from the amphoteric ion I. When there is a reducing agent such as formaldehyde, pyridine formate and aldehyde will be formed taking off a proton from the reducing agent.



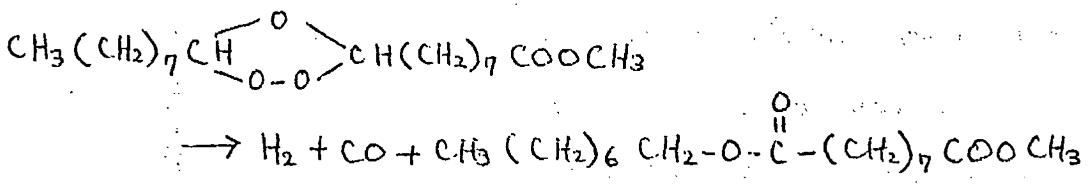
$$RCH{=}CHR \xrightarrow{O_3} \underset{\text{I}}{R\overset{\oplus}{C}HO\overset{\ominus}{O}} + RCHO$$

When pyridine was added before ozonization in methanol, the formation of acetal was prevented and the yield of dimethylester of azelaic acid was decreased markedly. In this case, there was no formation of pyridine oxide. It is assumed that the reason for this is that pyridine which is not associated with an amphoteric ion will make an addition complex with the solvent.

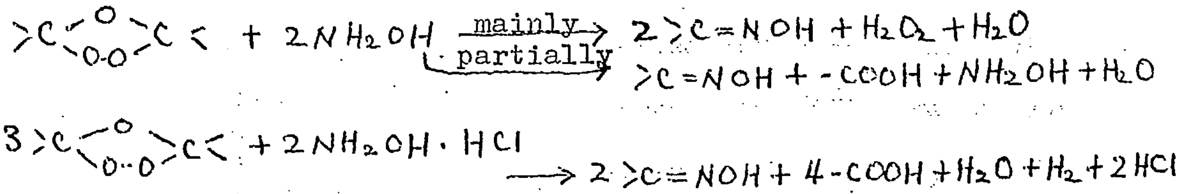
In 1958, Slomp et. al.[33] proposed a new theory such that an amphoteric ion will react with pyridine and produce a carbonyl compound and a pyridine oxide, which is quite different from Pryde's theory.



In 1963, the author et. al.[34] studied the decomposition of ozonide which was obtained by a reaction of ozone with crude methyl oleate under hydrogen pressure without using a solvent. The reaction proceeds smoothly at 29°C and the ozonide formed is quite different from an ozonide obtained in acetic acid and contains a very small amount of hydroxy peroxide. When it was heated to high temperature under hydrogen pressure, the following reaction appeared.



The reaction of ozonide obtained from the above reaction with hydroxyl amine was also studied as follows:



These reactions were compared with the decomposition reactions under hydrogen pressure.

6. Ozonolysis in order to obtain alcohols & amines

In 1956, the author[18] confirmed that it was possible to obtain alcohol directly from ozonide formed from oleic acid or methyl oleate in glacial acetic acid by hydrogenation at 150-232°C and at $100^{Kg}/_{cm^2}$, and that it was also possible to synthesis unsaturated hydroxy-glyceride from olive oil with the following procedure: olive oil was partially ozonized in acetic acid and the resulting ozonide was decomposed by heating, then glyceride was separated from the other products by steam distillation, and hydrogenated at 160-168°C and at $160\text{-}170^{Kg}/_{cm^2}$ for two hours in the presence of cupper-chromite catalyst. In this reaction ethylene bond remained almost unchanged and 64% of carbonyl radical converted to hydroxyl radical61).

In 1960, Sousa et. al.36) obtained 1-nonanol and 9-oxynonanoic acid in 63% and 43% recoveries respectively by reductive cleavage using a sodium borohydride catalyst after the ozonization of oleic acid in chloroform at -20°C. They also obtained 1-nonanol and 1,9-nonanediol in 79% and 50% recoveries respectively from the ozonide obtained from oleic acid in ethyl ether at 0°C by reductive cleavage in the presence of a lithium-aluminium-hydride catalyst. In 1962, Pollart et. al.37) obtained amines and amino compounds as main products from the ozonides obtained from oleic acid and methyl oleate in methanol by the reaction with liquid ammonia at 150°C with 2900 psi of hydrogen for 8 hours in the presence of Raney nickel. For example, from methyl oleate, n-nonylamine, methyl 9-aminononanoate, pelargonamide and stearamide were obtained in 44%, 52%, 33% and 15% yields respectively. In 1954, Otsuki et. al.38) obtained /P.447/ 350g of crude crystals of 9-aminononanoic acid as follows: sodium oleate, formed with 1 Kg of free oleic acid, dissolved in water was treated with ozone at 30-80°C, then hydroxylaminehydrochloride and pyridine were added to give oximes, and then the reductive cleavage took place in methanol using aluminium amalgam-water to yield the crude crystals. One Kg of methyl oleate was ozonized in glacial acetic acid at not higher than 15°C, decomposed by the addition of zinc powder, then fractionated and obtained 300g of methyl ester of azelaic acid half aldehyde, to which aqueous ammonia was added and reductive cleavage took place at 60-90°C, with 100 atm. of hydrogen for 3 hrs. using Raney nickel and obtained 280g of methyl 9-aminononanoate. They also obtained 10-amino capric acid, 9-aminononanoic acid and 9-aminononanoic acid triglyceride from undecylenic acid, ricinoleic acid, the fatty acid from rice bran oil and castor oil by similar chemical treatments as mentioned above. Oleic acid (100 parts) was ozonized in toluene at 0°C and the ozonide formed was added slowly to Na_2SO_3 aq. soln. and decomposed at 70°C; the resulting nonylaldehyde and toluene were steam distilled, then sulfuric acid was added to give azelaic acid half aldehyde, then reductive cleavage took place at 65-70°C with $100^{Kg}/_{cm^2}$ of hydrogen in the presence of Raney nickel catalyst to give 9-aminononanoic acid (27 parts). In 1962, Holmes39) obtained an aldehyde by reduction with zinc powder in glacial acetic acid after the ozonization of petroselinic acid in methanol at -10°C. Then hydroxylamine hydrochloride and sodium acetate were added to give oximes, then liquid ammonia was added and reduction was carried out at 95-105°C with 1000 lb. of hydrogen for 4 hrs. in ethanol to yield 48% dodecyl amine and 44% 6-aminohexanoic acid. In 1963, the author40) succeeded in obtaining oximes directly from ozonized methyl oleate by adding hydroxylamine hydrochloride and pyridine in methanol.

7. The application of ozonolysis techniques for glycerides 41)-45),60)

In an attempt to produce glycerides having multiple functional groups such as carbonyl groups, carboxylic groups, ethylene bonds etc., by partial ozonolysis of unsaturated fatty acids, the author41) studied the relationship between the decomposition conditions and the characteristics of the decomposition products using partially ozonized glycerides having different proportions of ozonization in glacial acetic acid, and also studied the reaction mechanisms in those decompositions.

The following are examples of the utilization of the partial ozonolysis techniques as applied to glycerides:

1) Reduction of carbonyl to alcohol, esterification with sulfuric acid, neutralization to obtain an alkali salt of an alkyl sulfate as the main product: surface active agent.

2) Carbonyl group converted to oxime, reduced to amine, treated with ethylene oxide, then esterified with sulfuric acid, neutralized and, as a final product, an amine type amphoteric surface active agent was obtained.

3) Carbonyl group treated to give acetal, and carboxylic group esterified, and as a final product, a plasticizer for use with polyvinylchloride. In 1961, Pryde et. al.[44)] studied a method for obtaining aldehyde type glycerides in good yield having multiple functional groups by ozonolysis of vegetable oil, and also studied their characteristics. That is; triolein was dissolved in a mixture of methanol and methylene chloride and ozonized at -4°C, then glyceride was obtained by reductive cleavage using zinc powder and glacial acetic acid. The yield of carbonyl group in the glyceride formed was 85%. On the other hand, with soybean oil the yield of carbonyl group found in the glyceride formed was only 72%. The soybean oil was dissolved in ethyl ether, ozonized at 10°C and then treated with hydrogen under normal pressure and at room temperature using a palladium-carbon catalyst for 7 hrs. to give the glyceride. (When isopropanol was used as a solvent, 40 psi of hydrogen pressure was necessary). These glycerides react with phenol, resorcinol, hexamethyleneglycol, urea etc. and form high polymers. In 1962, Pryde et. al.[45)] obtained mono- and di-aldehyde oils in good yield from the partial ozonides formed from vegetable oils by zinc reduction or by hydrogenation in the presence of pyridine. They also obtained the following results: Methyl linoleate was treated with 60% of the theoretical amount of ozone necessary to saturate the double bond and then reduced. The products from this reaction were 54% of methyl ester of azelaic acid half aldehyde, 18% of methyl 11-formyl-9-undecenoate and 28% of unreacted methyl linoleate. However, when the unreacted methyl linoleate was recycled,

with 60% of ozone consumption, the composition of the reactive product was 75% of methyl ester of azelaic acid half aldehyde and about 25% of methyl 11-formyl-9-undecenoate, and with 30% of ozone consumption, the yields were 68% and 32% respectively. When 30% of ozone is passed to the methyl linoleate, 24% of methyl azelaaldehydate, 12% of methyl 11-formyl-9-undecenoate and 12% of methyl ester of 14-formyl-9,12-undecadienoic acid were obtained as the reaction products. Tri, and di-aldehyde oils which have 2 or 3 aldehyde groups in one molecule or aldehyde acids such as azela-aldehydic acid, which should have been obtained in the reactions mentioned above, react with polyhydric alcohol, diamines and hydrazine and produce different kinds of high molecular-weight compounds. In 1963, Pryde et. al.60) obtained 34.55g of unsaturated aldehyde oil from 40g of soybean oil dissolved in 250 ml of ethyl acetae-ethanol(4:1) mixture. 40% of the double bonds were partially ozonized then hydrogenated at room temp. and under normal pressure using 0.1g of palladium-active carbon catalyst to yield the aldehydes. This unsaturated aldehyde oil had only 0.325 mole of aldehyde/mol of fatty acid: and unreacted olefinic unsaturation in the aldehyde oil was 0.342 mole/mole of fatty acid. However, when hydrogenation was carried out in the presence of 26.0g of pyridine after ozonation, the resulting unsaturated aldehyde oil (34.78g) had 0.329 mole of aldehyde/mole of fatty acid and 0.681 mole of unreacted olefinic unsaturation/mol of fatty acid.

/P.448/

8. Ozonolysis in an attempt to obtain azelaic acid

In Emery Industries46), azelaic acid was obtained in a good yield as follows: 100 parts of beef tallow, containing 92% of unsaturated fatty acid, dissolved in pelargonic acid, was ozonized at 25-40°C, then decomposition and oxidation were conducted by continuous blowing of oxygen for 6 hrs.: the resulting products were fractionated by distillation, extracted with hot water and finally 40 parts of pelargonic acid and 70 parts of azelaic acid were obtained. The authors47) obtained pure azelaic acid (mp 104.5 - 106.0°C) in a yield of 45-52% of theoretical recovery from oleic acid and rice bran oil fatty acid, which were ozonized in glacial acetic acid at 29°C, decomposed by heating. The acetic acid was removed by distillation and the decomposition products were oxydized by oxygen or by air in a heated cylinder, then extracted with hexane, and extracted with hot water to yield the pure final product. Otsuki48) obtained about 20g of crude azelaic acid from 50g of oleic acid as follows: 50g of oleic acid dissolved in butyl acetate was ozonized at below -5°C and the soln. was added by dropping into a steam distillation flask: pelargon aldehyde produced by the reaction and butyl acetate were removed by steam distillation: the residual mixture of pelargonic acid, azela-aldehydic acid and azelaic acid in the flask was ozonized with air or oxygen at 50-60°C for 4 hrs. and also at 95°C for 2 hrs. in the presence of manganese pelargonate catalyst, then extracted with hot water and obtained 20g of crude azelaic acid. Mihara et. al.49) obtained azelaic acid and pelargonic acid in good yields as follows: oleic acid was ozonized in acetic acid and decomposed to yield aldehyde-containing product, to which 20% manganese acetate acetic acid solution was added and oxygen was swept into the reaction flask to deepen the color of the reaction mixture: after deepening, the soln. was added to the ozonides and oxygen was swept in in order to decompose and to oxidize simultaneously. With the procedure above, they obtained azelaic acid and pelargonic acid in more than 75% recovery. Miyazaki et. al.50) treated 20g of oleic acid with 20g of water and ozonized at 40°C. After ozonation, oxygen was swept at 90°C and 65-70% of azelaic acid was obtained.

9. Ozonolysis in an attempt to determine the molecular Structures

One of the most important applications of the ozonolysis techniques in organic chemistry is in the identification of the molecular structures of unsaturated compounds. By the investigation of the ozonolysis products obtained from the unsaturated compounds, the position of ethylene bonds are determined and therefore the structures of the parent compounds are identified.

The structures of a large number of unsaturated fatty acids have been determined by the ozonolysis techniques. On the other hand, in 1951, Boer et. al.[51)] studied the use of ozone as a titrimetric reagent to determine the proportion of unsaturation of the olefinic unsaturated compounds. The principle of this method is as follows: Ozone is produced in high concentration by hydrolysis of diluted sulfuric acid, The ozone produced is conducted into the sample chloroform solution at a certain rate and the unsaturation of the sample is determined by the reaction time necessary to saturate the double bonds. The end point of the reaction was judged by the liberation of the unreacted ozone from the reaction system. It is assumed that the reaction of ozone in this system should be proceeded quantitatively. The presence of free ozone in the soln. was determined by the color change of the minute amount of the indicator added, but in many cases, the end point of reaction was confirmed by the iodometry which was carried out continuously to measure the amount of ozone released from the reaction vessel. From these data, the amount of ozone reacted was calculated. Indicators are: Ceroline Echtblauw R (Dutch Color & Chemical Works Limited, Sales Agent), Sudan Rot 7B (I.G. Farben, Sales Agent), Bordeaux Organol M and Ecarlate Organol (Ste. Anne des Matieres Colorantes Saint-Denis, Sales Agent). In the case of undecylenic acid, oleic acid and castor oil, Sudan Rot 7B was used as an indicator and almost the same values were obtained as the Bromine values of those compounds. In 1961, Maggiolo et. al.[53)] simplified the method established by Boer et. al.[51)]. As an ozonizer, they used a simple model available commercially, and which produced 15-20$^{mg}/_{min.}$ of ozone from air.

Concentrations of ozone, before and after the reaction, were determined by the amounts of ozone reacted with 2% KI aq. solns, for measured 3 minutes. A sample, which should contain 6-7 milli. equivalents of ethylene bonds, was taken in a reaction vessel equipped with a stirrer at 2500 rpm, then 35 ml of chloroform was added to dissolve the sample and then the solution was cooled to -45- -55°C. The end point was indicated by the appearance of a blue color in the reaction soln. due to the excess of ozone and simultaneously, by the appearance of a distinct yellow color in the potassium iodine soln. which was connected next to the reaction vessel. However, since these end points consistently appeared 0.4 min. earlier than the real end points, correction was required. The amount of ozone absorbed by 100g of sample was calculated from the time needed to complete the reaction. The result was expressed as "ozone value", which is the number of grams of ozone absorbed per 100g of sample. The reproducibility of ozone value was very good. The ozone values obtained from methyl oleate, linoleic acid, methyl linolenate, olive oil, sesame oil, safflower oil and tall oil showed the corresponding values to the Iodine values by the Wijs method. When the rate of ozone absorption of sample was very slow, it was possible to obtain a definite end point using an ozone reaction curve which was plotting ozone concentration versus time. In 1961 Ackman et. al.[25)] studied a method to oxidize oleic acid by 98%-formic acid and hydrogen peroxide (30-50%) after ozonization at -30°C in methanol (mentioned above). In this method, the yield of azelaic acid was more than 95% and the reaction bi-products were very little. More bi-products were obtained when acetic acid - methyl formate (3:1), acetone or methyl formate was used as the reaction solvent than when methanol was used. This method was excellent as a method of quantitative analysis of ethylene bonds in the long chain unsaturated mono fatty acids. In 1962 Privitt et. al.[58)] studied a method of identification of structures of unsaturated fatty acids using acetaldehydes which were obtained by the reductive decomposition of ozonides by the gas chromatographic techniques as follows: 10 ml of purified pentane was taken in a 25 ml round-bottom flask, ozonized oxygen containing 2-3% of ozone was passed through at a rate of 100 ml/min. for 5 min. to give a deep blue soln. containing about 0.3 m mol of ozone. On the other hand 1-50 ml of sample was dissolved in purified 2-3 ml of pentane, cooled to a proper temperature, so that the sample does not crystalize, and the soln.

was added to a 10 ml of ozone soln. As the reaction takes place momentally, excess oxygen and ozone are removed by using an aspirator. When the ozonization is completed, the color of the soln. should be faint grey. If the soln. is colorless, it means that the ozone is not sufficient, so the ozonized oxygen should be passed into the soln. until the color changes to faint blue. Before the decomposition, the ozonide soln. is usually concentrated to approximately 2 ml. If the sample produces short chain compounds the concentrating procedure should be carried out under a reduced pressure at 0°C. The esters which show relatively long retention time (Rt) in gas chromatography, such as methyl caprylate or methyl phthalate, were used as the solvents when reduction was carried out. The reduction method is as follows: To avoid the secondary oxidation of aldehydes which were produced by the cleavage of the ozonide, the whole unit should be kept away from oxygen. 25 mg of palladium catalyst by Lindar[54)] and 2 ml of solvent were taken in a flask, cooled with ice cold water, and then stirred vigorously using an electromagnetic stirrer under a stream of hydrogen. A sample was dissolved in a small amount of solvent in a test tube and the solution was saturated with hydrogen. Under a current of hydrogen gas, sample was taken into a reaction flask using a syringe. The reaction flask was tightly sealed and pressured with hydrogen. The reaction should be completed in 15 min. The decomposed products were warmed up with a water bath and the volatile materials in the products were liberated with nitrogen and the liberated materials were collected in heptane which was cooled with dry ice or in 0.5 ml of non volatile hydrocarbons taken in a U shaped-tube. The solutions in the collection tube and in the reaction flask are analysed by gas chromatography. Columns used are 30% silicone on Chromosorb W, 12 ft. x $\frac{1}{4}$ inch and 15% succinic acid ethylene glycol polyester on Chromosorb W, 6 ft. x $\frac{1}{4}$ inch. A hydrogen flame detector was used for the analysis. With this method, when methylesters of linoleic acid, linolenic acid and arachidonic acid, methyl oleate containing 2% of linoleic acid, a mixture of methyl oleate and methyl petroselinate were used as samples, clear separations of aldehydes obtained by the cleavage of these samples were achieved. Since this method is not accompanied with the subreactions in both ozonation and reduction procedures, and does not include a separation procedure, in which usually the largest sample loss will be seen, it is possible to use this method as a method of quantitative analysis of mixture of the esters of unsaturated fatty acids. The most important fact in the method is, however, that it is possible to analyse quantitatively the mixture of the structural isomers of the unsaturated fatty acids. It is impossible to analyse in the ordinary gas chromatographic technique.

10. Ozonizers and Prices of Ozone

The method of ozone production in industry is mainly by the silent discharge of air or oxygen. There are two types of silent discharge tube; one is a disk type and the other is a cylindrical type. The disk type; M.P. Otto model is famous for its use as a sterilizer for water supplies in France. In the cylindrical models, the Vermont is used in water cleaning equipment in Philadelphia and the Welsbach model of the Emery Industries is being used for azelaic acid production. Theoretically, the necessary power to produce 1 Kg of ozone is only 0.8 KW.hr, but in practice by the Welsbach model, 18-22 KW.hr. with air and 9-11 KW.hr. with oxygen are necessary. It is possible, however, to reduce the power to 12-15 KW.hr. with air by adjustment of the discharge distance or thickness of a dielectric substance. In 1957 Funabashi et. al.[56)] succeeded in reducing the power to 8-9 KW.hr. to produce 1Kg of ozone using a metal electrode as one of the electrodes of the silent discharge tube. The surface of the electrode is covered with a thin film (less than 0.5 mm) of organic synthetic resin to be used as a dielectric substance. In Toyo Koatsu Kogyo K.K.[55)] (Toyo High Pressure Industry Co. Ltd.), they succeeded in obtaining ozone in a very high efficiency using a special device which is designed to recycle the recovered oxygen. The largest equipment in the Welsbach Company can produce 86$^{Kg}/_{day}$ of ozone from air and 172$^{Kg/}$day from oxygen and concentrations are 1 and 2% respectively. Cost for the equipment was 14,400,000 yen (U.S. $40,000) and cost 3,600,000 - 5,400,000 yen (U.S. $10,000 - 15,000) for the fan, cooler, drier etc. The Welsbach Company is planning to produce pure ozone at 119 yen/Kg (approximately U.S. $ 0.33) and the Mathieson Company is planning to produce and to sell 100% pure ozone. In the Union Carbide Corp. Linde Div., there has been a special study to stabilize 24-35% of ozone in liquid oxygen as a high concentration ozone solution. The Emery Industries Co. was using a large piece of equipment which cost 720,000,000 yen (U.S. $2,000,000) for production of azelaic acid. In June 1961, they completed a larger unit which cost 2,160,000,000 yen (U.S. $6,000,000).

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