



TITLE:

On the Addition of Oxygen to the Double Bonds

AUTHOR(S):

Tanaka, Shozo

CITATION:

Tanaka, Shozo. On the Addition of Oxygen to the Double Bonds. Memoirs of the College of Science, Kyoto Imperial University. Series A 1939, 22(3): 97-127

ISSUE DATE:

1939-05-31

URL:

<http://hdl.handle.net/2433/257216>

RIGHT:

On the Addition of Oxygen to the Double Bonds

By Shozo Tanaka

(Received April 14, 1939)

One of the attractive themes in the fields of organic and biochemistry is the study of the synthesis of oxygen compounds from unsaturated compounds by the addition of oxygen to the double bonds with a view to the industrial utilization of oxygen and also for the better understanding of oxidation occurring in the living cells.

With regard to the synthesis of oxygen compounds from corresponding unsaturated hydrocarbons, two representative methods have been known, one of which is the method of introducing primarily halogen molecules into double bonds of hydrocarbon and then converting the addition compounds thus formed into the corresponding oxygen compounds; and the other is the method of direct oxidation of the double bonds. The latter is further divided into the following two—the direct addition of oxygen to the double bonds and oxidation by the inorganic or organic peroxides.

For the purpose of investigating the reaction of oxygen addition to the double bonds, p-menthene Δ_3 , which shows the properties of B. p.=168-169.5°, $d_4^{25}=0.8107$, $n_D^{25}=1.4487$, M. R.=45.63 (calculated value for $C_{10}H_{16}O=45.71$) and $[\alpha]_D=+107.24^\circ$, and benzaldehyde, which indicates the properties of B. p.=(77-79°)₁₈, $d_4^{25}=1.0409$ and $n_D^{25}=1.5425$, were oxidized by organic peroxides such as peracetic acid, perbenzoic acid and menthene ozonide and also by inorganic peracids.

However, between menthene and menthene ozonide, no reaction was seen to take place even when they were heated at 170°C for a long while, though when the known quantity of menthene was added drop by drop into chloroform or ether solution of peracetic or perbenzoic acid with vigorous agitation under ice-cooling, rapid decrease in the available oxygen content of the solution occurred and the total amounts were exhausted in 8 hours in the case of chloroform solution, but in 150 hours when ether was used as the solvent. Hereupon, the organic acids were removed from the solutions by shaking them with dilute caustic soda and the solvents were carefully distilled off. By rectification of the residual liquid, a compound which shows the following physical properties was obtained with a good yield:

$$\text{B. p.} = (74-75)_{\text{H}}, \quad d_4^{25} = 0.8946, \quad [\alpha]_{\text{D}} = +53.17^{\circ}$$

$$\begin{array}{cccc} n_{\alpha}^{25} & n_{\text{D}}^{25} & n_{\beta}^{25} & n_{\gamma}^{25} \\ 1.44369 & 1.44595 & 1.45148 & 1.45502 \end{array}$$

	M_{α}	M_{D}	$M_{\beta} - M_{\alpha}$	$M_{\gamma} - M_{\alpha}$
Observed value	45.76	45.96	0.69	1.01
Calculated value for $\text{C}_{10}\text{H}_{18}\text{O}$	45.43	45.62	0.67	0.99
E. M.	+0.33	+0.34	+0.02	+0.02
E. Σ .	+0.21	+0.27	+3%	+2%

Molecular heats of combustion

	1302.8 K		302.5 K
The present substance $\text{C}_{10}\text{H}_{18}\text{O}$	1278.7	Ethylene oxide $\text{C}_2\text{H}_4\text{O}$	279.3
r-Menthone $\text{C}_{10}\text{H}_{18}\text{O}$		Acetaldehyde $\text{C}_2\text{H}_4\text{O}$	
Difference	24.9	Difference	23.2

Parachor

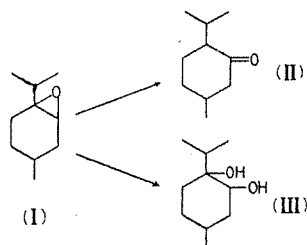
	$\frac{M}{D-d} \gamma^{1/4}$	$\Sigma(P)$	Difference
The present substance	396.1	381.9	+14.0
r-Menthone	400.9	405.1	- 4.1
Ethylene oxide	112.5	98.0	+14.5

From the results of elementary analysis ($\text{C}\% = 77.75$, $\text{H}\% = 12.04$ against the calculated value for $\text{C}_{10}\text{H}_{18}\text{O}$, $\text{C}\% = 77.85$, $\text{H}\% = 11.77$), the present compound thus obtained was presumed to consist of the oxygen compound $\text{C}_{10}\text{H}_{18}\text{O}$ produced by the addition of one atom of oxygen to menthene. And in the results shown in the above table, it is noted that the observed value of molecular refractivity and the molecular heats of combustion and parachor differ from those of menthone which has the same molecular formula. It is noticeable that these differences are almost the same as those observed between acetaldehyde and its isomer ethylene oxide; therefore the existence of ethylene oxide ring in the present molecule may be assumed.

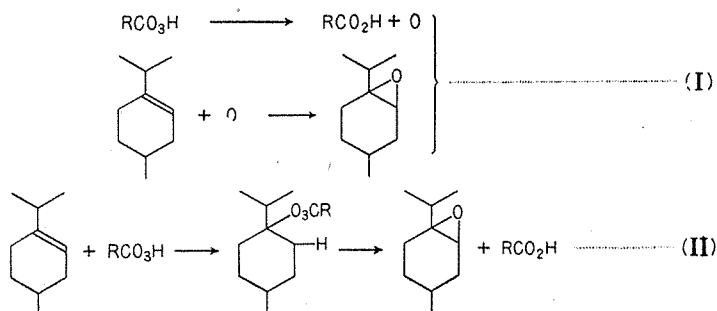
This compound was proved to be composed of menthene oxide-3.4 (I) by the following facts: by the action of alumina or sulphuric acid at high temperatures, this compound transformed into i-menthone (II); it showed properties (B. p. = 205-209°, $d_4^{25} = 0.8943$, $n_{\text{D}}^{25} = 1.4567$, $[\alpha]_{\text{D}} = \pm 0$, semicarbazone melting at 209° and oxime melting at 79-80°) which had been produced by the reduction of p-menthene-1-on-3,¹⁾ and by the action of dilute sulphuric acid in cold, the formation of menthene-glycol-3.4 (III); it showed properties (B. p. = (129-135°)_H

M. p. = 75-76°) which had been prepared from menthene- Δ_3 by oxidation with potassium permanganate,²⁾ occurred.

In general, ethylene oxide compounds have been produced by the oxidation of the ethylenic compounds with organic peracids.³⁾



However, it was desirable to learn whether the formation of ethylene oxides may be caused by the addition of active oxygen liberated from peracids, as shown in formula (I), or by reactions according to formula (II); the latter would mean that primarily the formation of an unstable ester-like additional compound may take place with the addition of a peracid molecule to the ethenoid linkage, and then the decomposition of this compound into ethylene oxides may follow. For discriminating between these two and also to examine the evolution of active



oxygen by decomposition of peracids, the rate of decomposition of peracids in chloroform and of the corresponding sodium salts in an aqueous solution at 30°C were investigated by measuring the decrease in available oxygen content by iodometry.

As shown in Figs. 1, 2 and 3, both perbenzoic and peracetic acids are relatively stable in the chloroform solution, but their salts decompose rapidly into the corresponding organic acids and oxygen molecule. In these experiments the potassium iodide-starch paper hung in the space of the vessels containing free peracids soon turns blue, while the paper hung over the salt solution shows no sign of colouring, therefore, it seems to be the reverse results against the degree of self-decomposition.

The decrease in available active oxygen in the solution of peracid with a definite amount of menthene, is shown in Figs. 1, and 3, and it is followed by the formation of menthene oxide, but in the case of

Fig. 1. Perbenzoic acid (available oxygen content 0.0564 g)

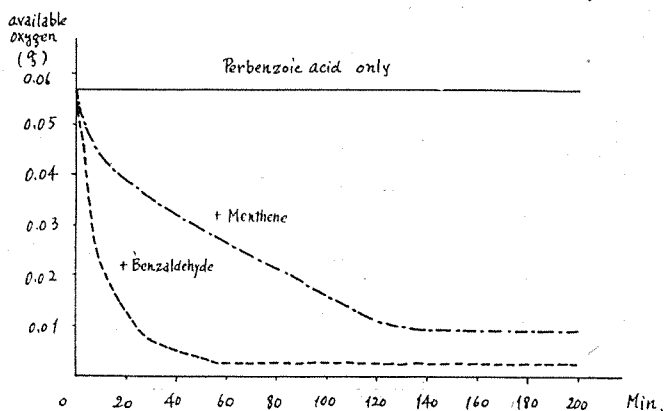


Fig. 2. Sodium perbenzoate (available oxygen content 0.0228 g.)

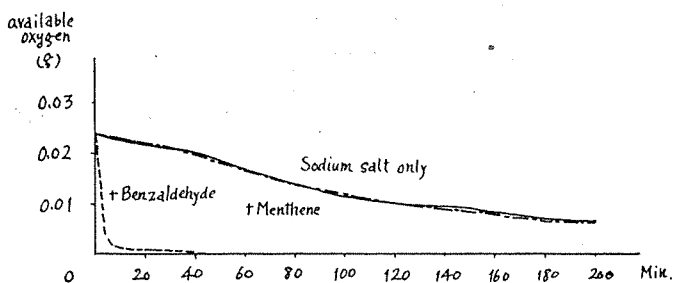
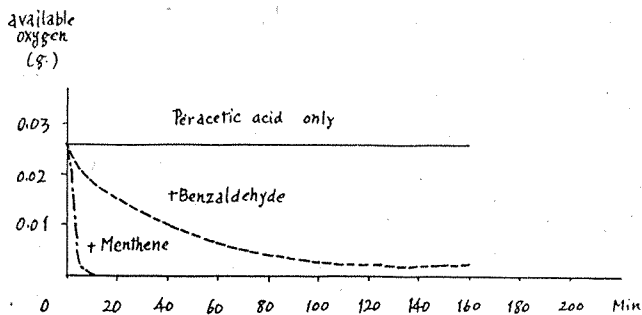


Fig. 3. Peracetic acid. (available oxygen content 0.0259 g)



the salt solution with menthene, the rate of decrease of available oxygen is identical with that by natural decomposition, as shown in the figure, and almost the total amount of menthene used was recovered.

These results show that oxygen liberated by the decomposition of

peracids may be composed of inactive molecular oxygen and the blue colouration of the test paper in the case of free peracids may be attributed to the vapour of peracids.

Consequently, the formation of ethylene oxides by the action of peracids on the ethylenic compounds is presumed to occur according to the mechanism expressed by formula (II).

Now, with the object of confirming the intermediary formation of labile ester of peracids, oxidation of menthene molecule was undertaken by inorganic peracids, such as Caro's acid, hypochlorous acid and hypoiodous acid.

With Caro's acid, prepared from potassium persulphate and conc. sulphuric acid, no sign of oxidation of menthene was observed.

In the case of hypochlorous acid, equivalent amounts of menthene and the solution of sodium hypochlorite were mixed together and with vigorous stirring zinc sulphate solution was added drop by drop into the above mixture until available oxygen was completely exhausted. After extraction of the reaction products with ether and distillation of the solvent, pale yellowish dense liquid was obtained which was presumed from its properties to consist of menthene chlorohydrin.

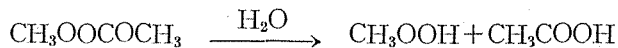
Oxidation of menthene with hypoiodous acid was performed as follows: a mixture of calculated amounts of red mercuric oxide and ether solution of menthene with a small amount of water was agitated vigorously under cooling; into this mixture powdered iodine was thrown bit by bit until the violet colour of iodine remained without fading, and then the precipitate of mercuric iodine formed was filtered off; and from the ether layer a colourless dense liquid was gained which gradually became tinged with red by the liberation of iodine.

This compound was presumed to consist of menthene iodohydrine because cyclohexene iodohydrine⁴⁾ has been prepared by a similar method.

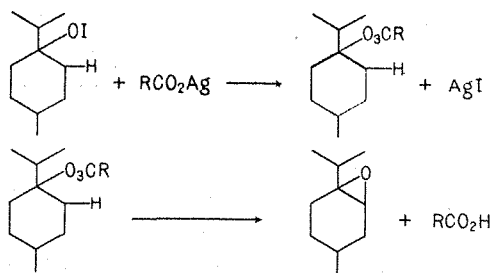
Without attempting refinement of halogen hydrines because of their instability, elimination of hydrogen halides from them by powdered caustic potash was carried out and menthene oxide-3,4 was proved to be produced with yields of 30~60%.

Thus for the purpose of synthesizing perbenzoic or peracetic esters of menthol from menthene iodohydrine, an alcoholic solution of iodohydrine was boiled on a water bath for a long while with powder of silver benzoate or silver acetate. By this treatment, instead of the formation of esters, menthene oxide-3,4 was obtained with a yield of 30% by silver benzoate and of 35% by silver acetate respectively, as well as almost equal amounts of the corresponding free acids.

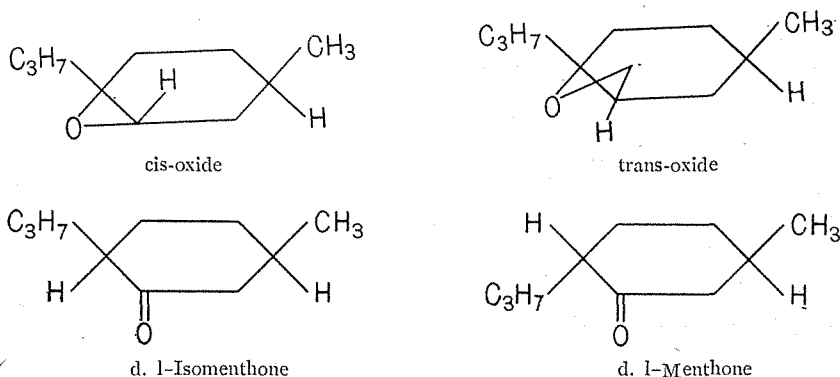
These facts prove that the intermediately formed esters may be very unstable and at once decompose into menthene oxide and the free acids. And also, the results of the previous investigation reported by A. Baeyer and V. Villigar⁹⁾ that methylester of peracetic acid was hydrolyzed into methyl-peroxide and acetic acid immediately in the aqueous solution as shown below, were in favour of the writer's presumption.



Consequently, the formation of ethylene oxide by the oxidation of the ethylenic linkage with peracids, may follow the reaction shown in the above equation. (II).



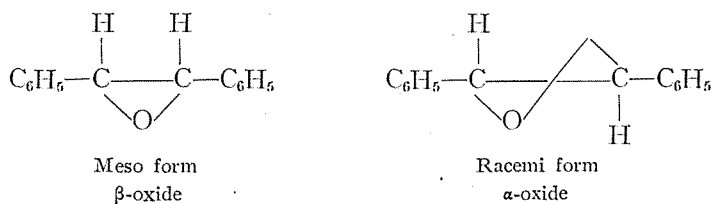
In addition to the foregoing, the existence of the trans-cis geometrical isomers in menthene oxide may be reasonable.



By the action of dilute sulphuric acid or alumina, menthene oxide was proved to be converted into *i*-menthone⁹⁾ consisting of equal amounts of *d. l*-menthone and *d. l*-isomenthone. These facts indicate the ostensible intermixing of equal amounts of *cis*- and *trans*-isomers in original menthene oxide, but as easy intermolecular rearrangement between menthone and *iso*-menthone by the action of heat or acids

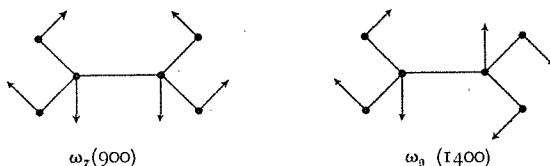
has been reported by numerous investigators,⁷⁾ the original ratio in the geometrical isomers of menthene oxide has not yet been definitely determined.

Therefore, in order to determine the ratio of trans- and cis-isomer of ethylene oxides directly, the isolation of geometrical isomers from stilbene oxide prepared in the same way, was performed. In this experiment, not only the amount of trans-cis isomers formed, but also the time required for the completion of the reaction were strikingly affected by the difference of the solvent used as shown in the following table.



Sample	Oxidizing agent	Solvent	Time required for completion of reaction	Reaction products
Stilbene 20gr.	Peracetic acid	Ether	200 hr.	100% α -Oxide
Stilbene 20gr.	Peracetic acid	Chloroform	19.5	{ 94% α -Oxide { 6% β -Oxide

These results are analogous to those of the investigations on the difference in effects of the different solvents and also those on the effect of irradiation: the ratio of α -dibromide and β -dibromide of stilbene has been altered in bromination⁸⁾ apparently because of the light-filtering action of the solvent⁹⁾ through which light of the frequency corresponding to ω_7 and ω_9 vibration in stilbene molecule may pass.



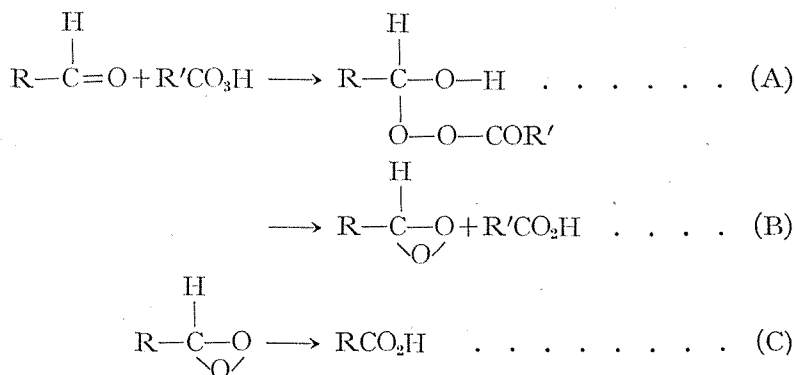
The formation of the different amounts of α - and β -oxide of stilbene by the action of peracids is also explained as the effect of the same cause, but it is an interesting problem for future study whether the marked disparity in the reaction velocity with the difference of the solvent used should be ascribed to the effect of the photochemical properties of the solvent, or whether it may be caused by other properties such as polarity, etc.

It is well known that in physical properties there is a close resemblance between the ethylenic and carbonyl linkages as shown in the table, and that in chemical properties they resemble each other in the tendency to polymerization, autooxidation and addition-reaction of other compounds to these double bonds.

	C=C	C=O
Parachor ¹⁰⁾	23.2	23.0
M _D ¹¹⁾	1.7	2.2
Raman effect ¹²⁾	1630 Å	1722 Å
Ultraviolet absorption band ¹³⁾	2700 Å	2700-2800 Å

To return to the experiments: the research on the addition of oxygen to the carbonyl linkage was made by slowly dropping chloroform solution of benzaldehyde and acetaldehyde into the cold solution of peracids, and acidimetry tests proved that the theoretical amount of benzoic acid in the former case and of acetic acid in the latter, had been formed.

In these cases, the formation of the acids corresponding to aldehydes may be caused by reaction analogous to the cases of oxidation of ethylenic compounds and the addition of the peracid molecule to the carbonyl linkage may occur primarily followed by the decomposition of the addition compounds into aldehyde peroxides which in turn, may transform into the corresponding acids by intermolecular rearrangement, as shown in the following schemes:



The formation of the addition compound (A) is presumed to be due to the same cause which produces the analogous tendency of aldehydes to form the addition compounds of ammonia, hydrogen cyanide and sodium bisulphite, but the facility of decomposition of the addition compounds (B) may depend upon their own stability.

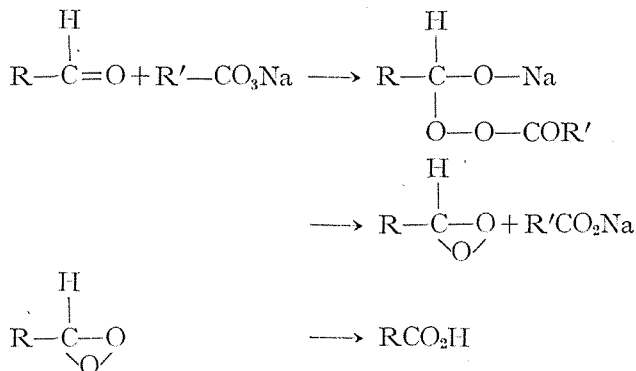
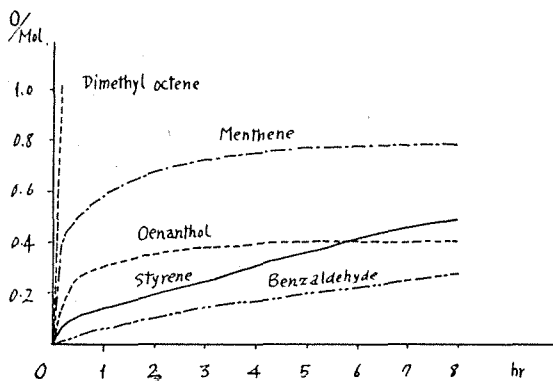
Thus, the addition of oxygen to the ethylenic and also carbonyl double bonds takes place by the same mechanism as has been mentioned above, but perhaps they differ from each other in reactivity. In order to investigate the reactivity of these double bonds, the reaction velocity of oxidation of 2,6-dimethyl octene Δ^6 , p-menthene Δ^3 , styrene, oenanthal, and benzaldehyde with peracetic acid was studied. The $N/2$ chloroform solution of each sample was mixed with the known quantity of peracetic acid at 0°C and the amount of available oxygen remaining was estimated at definite intervals by iodometry. As shown in Fig. 4, the action of peracid always takes place more rapidly on the ethylenic compounds than on the corresponding carbonyl compounds, as is seen in the case of styrene and benzaldehyde.

Moreover, among ethylenic and also among carbonyl compounds, there are marked difference in the reaction velocity according to the molecular structure.

However, the oxidation of carbonyl compounds by peracid is brought about far more slowly than that

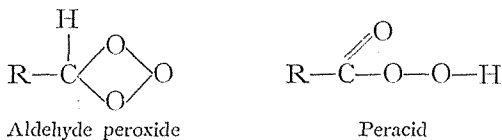
of ethylenic compounds, and the former differs from the latter in the characteristic that it is oxidized by sodium salt of peracid. This reaction is supposed from the analogy with the case of free acid to follow the mechanism shown below.

Fig. 4.



Moreover there may be a close resemblance between the oxidation of aldehydes by peracid or its salt and the autooxidation of aldehydes. When aldehydes are oxidized to the corresponding organic acids automatically by the action of aerial oxygen, it has been ascertained that the peroxides are found as the result of the intermediary addition of oxygen molecules to aldehydes.

With regard to this presumptive peroxide, A. Bach¹⁴⁾ holds that it may be aldehyde peroxide, though C. Engler and W. Wild,¹⁵⁾ H. Staudinger,¹⁶⁾ H. Wieland,¹⁷⁾ P. van der Beek,¹⁸⁾ and E. Reymond¹⁹⁾ maintained that it was peracid itself, and the latter opinion was partly confirmed by the isolation of perbenzoic acid produced by the autooxidation of benzaldehyde.



Concerning this view, the writer investigated the autooxidation of benzaldehyde in the air by measuring the pressure decrease manifested on the mercury manometer attached to a vessel of definite volume, in which the known quantity of benzaldehyde and peracids or menthene ozonide are contained. The results are shown in Figs. 5 to 8.

As may be seen in the figures, the oxidation of benzaldehyde by peracids or by their salts was accomplished very quickly and seems to take place apart from the autooxidation, while, when ozonide is used as the oxidizing agent, the aldehyde is oxidized at a slow rate by the ozonide rather than by autooxidation.

Fig. 5. Perbenzoic acid (available oxygen content 0.0151 g.)

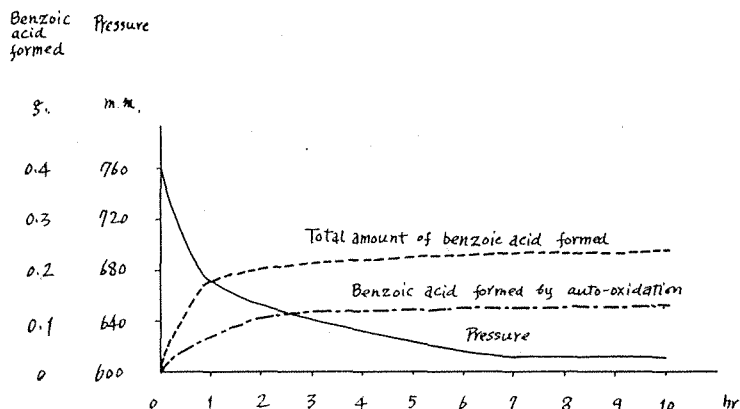


Fig. 6. Sodium perbenzoate (available oxygen content 0.0301 g)

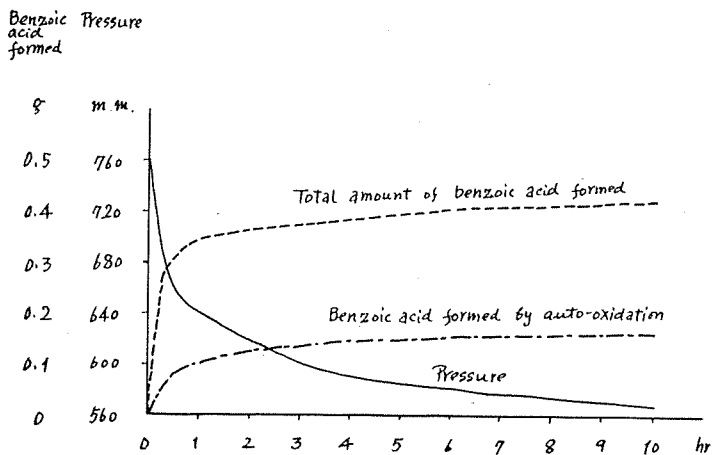


Fig. 7. Peracetic acid (available oxygen content 0.0386 g)

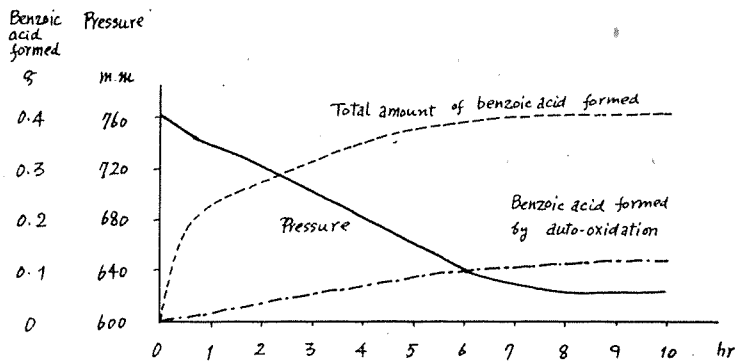
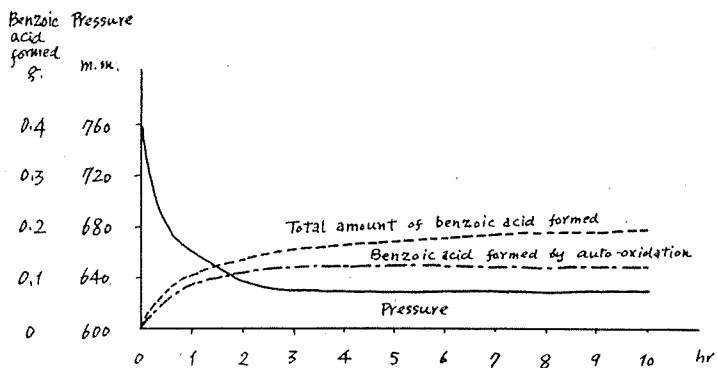
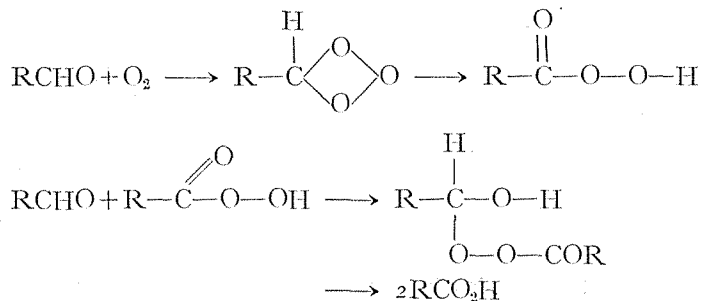


Fig. 8. Menthene ozonide (available oxygen content 0.0138 g)

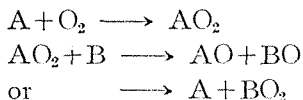


Moreover, the blue colouration of potassium-iodide starch paper over benzaldehyde was noticed likewise in the cases of peracide, but over the ozonide solution no sign of tinging was observed.

From these facts, the writer came to the opinion that in the progress of the autooxidation of aldehydes, the intermediary formation of the corresponding peracids according to the following schemes is probable:



In general, the substrates subjected to biological oxidation are composed of the compounds which contain carbonyl or ethylenic linkage in their molecules, such as carbohydrates and fatty acids, and the oxygen donators are supposed to consist of the inorganic²¹⁾ and the organic peroxides²²⁾ and the oxidation of the substrate by the oxygen donator seems to take place as follows²³⁾:



A: Autooxydator

AO₂: Oxygenase

B: Substrate

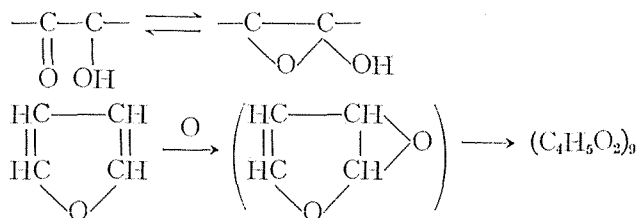
The isolation of a peroxidase-like substance²⁴⁾ with the properties of aldehyde peroxide²⁵⁾, which was lately confirmed to be identical with peracid itself²⁶⁾, led to the assumption of the probable correlation between peroxidase and the aldehydes in the cells.

This deduction was strongly supported by the writer's findings, which suggest the significance of the formation of peracid-like substance by the autooxidation of carbonyl compounds.

Apart from these problems, the easy polymerization of ethylene oxide compounds was observed. When menthene oxide was heated to 100°~120°C for 20 minutes with a drop of acetic acid, 25% of the oxide was converted into a brown coloured viscous matter which was

proved by the results of elementary analysis to consist of the polymer of menthene oxide.

M. Bergmann²⁷⁾ attributed the tendency to polymerization of acyloin linkage to the probable formation of ethylene oxide ring by tautomeric change and J. Böeseken²⁸⁾ noticed the occurrence of the unavoidable polymerization of the oxidized products of furan and its derivatives by peracetic acid.



These results may offer a cogent argument concerning the natural formation of starch, cellulose and other gummy matters in connection with the facts of the thermal polymerization of anhydro-sugars,²⁹⁾ which contain the ethylene or butylene oxide ring in the molecule.

Besides, the ready transformation of ethylene oxide compounds into ketone, the reduction into alcohol, and the hydration into glycol were precisely investigated³⁰⁾ and the results obtained also furnish suggestions for explanation of the formation of natural alcohols and also ketones in the cells.

Experimental part

§ The preparation of p-Menthene Δ_3 .

p-Menthene Δ_3 used as material in the present investigation was prepared from menthol by catalytic dehydration. Over a thin layer of alumina heated to 300°C, the vapour of menthol was passed at the rate of 10 gr. per hour. The reaction product separated from water, was dried with anhydrous Glauber's salt and distilled with metallic sodium. The racemization of menthene by repetition of dehydrating treatment was noticed. The yield of menthene, the physical properties and the results of elementary analysis are shown as follows :

No	Menthol	Passed on heated Al ₂ O ₃	Yield of menthene
I	195 gr.	once	139 gr. (81%)
II	212	thrice	178 (84%)

No.	B. p.	d_4^{25}	n_D^{25}	$[\alpha]_D$	M. R.	$C_{10}H_{18}F_1$
I	168°-169.5°	0.8107	1.4487	+107.24°	45.63	45.71°
II	167°-168°	0.8109	1.4490	+ 41.30°	45.65	

No.	Sample	CO ₂	H ₂ O	C%	H%
I	0.1317 gr.	0.4189 gr.	0.1599 gr.	86.75	13.59
II	0.1726	0.5504	0.2067	86.79	13.40
$C_{10}H_{18}$				86.96	13.04

§ The oxidation of menthene by menthene ozonide.

10 gr. of menthene was dissolved in 10 times its volume of chloroform and ozonized air was passed under ice-cooling. After the reaction came to an end, the solvent was distilled off in vacuo and the residual jellied ozonide was washed several times with petroleum ether. The ozonide thus obtained was mixed with 10 gr. of menthene and heated to 170° for a long time under a reflux condenser. The reaction product was distilled under diminished pressure to obtain 87% of unchanged menthene showing the properties of B. p.=(62-63°)₁₄, d_4^{25} =0.8111 and n_D^{25} =1.4493.

§ The oxidation of menthene by perbenzoic acid.

The sodium salt of perbenzoic acid was prepared from benzoyl peroxide and sodium alcoholate by J. Levy and R. Lagrave's method.³¹⁾ After liberating free acid by acidification with the cautious addition of dilute sulphuric acid, the free acid was extracted with chloroform. Under ice-cooling, the calculated amount of menthene for the available oxygen content of peracid solution was slowly dropped with vigorous stirring. When the available oxygen was completely exhausted, the solution was extracted with dilute alkali to remove the free acids, and the solvent was distilled off. The residue was rectified carefully and some quantity of a fragrant liquid of the following properties was obtained :

Sample	Solvent	Time required for completion of reaction	Yield	B. p.	d_4^{25}	n_D^{25}	$[\alpha]_D$
Menthene I 20gr.	Chloroform	7.5 hr	91%	(63-73°) ₁₃	0.8933	1.4460	+53.97°
Menthene II "	"	8.5	85	(78-80°) ₁₅	0.9013	1.4460	+22.72°
Menthene I "	Ether	122	83	(77-79°) ₁₅	0.8992	1.4458	+51.99°
Menthene II "	"	173	87	(78-80°) ₁₅	0.8989	1.4454	+23.01°

§ The oxidation of menthene by peracetic acid.

Peracetic acid was prepared by B. Arbusow and B. Michailow's

method.³²⁾ With a trace of sulphuric acid as the stabilizer the calculated amount of 50% hydrogen peroxide was dropped into cold, freshly distilled acetic anhydride under vigorous agitation and the mixture was left to stand for 2 days in the ice-box. The solution was carefully fractionated under the pressure of 14 mm. and the fraction distilled at (30~35)₁₄ was collected, which was proved to consist of about 60% peracetic acid and 40% acetic acid. The oxidation of menthene by the peracetic acid thus obtained was carried out as in the case of perbenzoic acid and a sweet-smelling liquid of the following properties was obtained :

Sample	Solvent	Time required for completion of reaction	Yield	B. p.	d ₄ ²⁵	n _D ²⁵	(α) _D
Menthene I 20 gr.	Chloroform	10.5 hr	80%	(69-71°) ₁₃	0.9000	1.4461	+53.00°
" II "	"	8.0	89	(78-81°) ₁₅	0.9008	1.4468	+20.97°
" I "	Ether	182	59	(74-76°) ₁₄	0.8956	1.4456	+52.85°
" II "	"	152	76	(82-87°) ₁₇	0.9002	1.4466	+22.72°

§ The properties of menthene oxide-3,4.

The oxidation products obtained by the reaction between menthene (I) and peracids were mixed together and rectified. The physical properties of the refined liquid were precisely investigated. The results of the measurement of molecular dispersion, of the heat of combustion, of parachor and also elementary analysis are shown below :

B. p. = (74-75°)₁₄, d₄²⁵ = 0.8946, n_D²⁵ = 1.4460, [α]_D = +54.21

Measurement of molecular dispersion and calculation of E-value.³³⁾

	n _α ²⁵	n _D ²⁵	n _β ²⁵	n _γ ²⁵
	1.44369	1.44595	1.45148	1.45502

	M _α	M _D	M _β - M _α	M _γ - M _α
Observed value	45.76	45.96	0.69	1.01
Calculated value	45.43	45.62	0.67	0.99
E. M.	+ 0.33	+ 0.34	+ 0.02	+ 0.02
E. Σ.	+ 0.21	+ 0.21	+ 3%	+ 2%

$$n_D^{20} = 1.44801$$

$$n_D^{20} \times M$$

Observed value 223.28

Calculated value 230.12

E-value 6.84

E-value for trimethylene ring 5.50

Measurement of the heat of combustion. The heat of combustion of the present substance was measured by Berthelot's bomb and the results thus obtained were compared with that of menthone in accordance with the difference between ethylen oxide³⁴⁾ and acetaldehyde.³⁵⁾

Sample	Water equivalent	$\Delta^{\circ}\text{C}$	gr. heat of combustion	Molecular heat of combustion
0.7995 gr.	2097 C	3.228 ^o C	8460 C	
0.6311	2097	2.545	8450	
0.5597	2097	2.262	8468	
Average			8460	1302.8 K

r-Menthone	Water equivalent	$\Delta^{\circ}\text{C}$	gr. heat of combustion	Molecular heat of combustion
0.6163 gr.	2097 C	2.445 ^o C	8313 C	
0.5852	2097	2.316	8294	
Average			8303	1278.7 K

	gr. heat of combustion	Molecular heat of combustion
The present substance	8460 C	1302.8 K
r-Menthone	8303	1278.7
Difference	157	24.9

	gr. heat of combustion	Molecular heat of combustion
Ethylene oxide	6870 C	302.5 K
Acetaldehyde	6338	279.3
Difference	532	23.2

Measurement of parachor. From the values of the surface tension of the present sample measured by the capillary method (radius 0.0447 cm) and of the density at various temperatures, parachor was calculated by the equation offered by S. Sugden. The results are shown in the following table. On comparing these results with those of menthone the existence of ethylene oxide ring in this substance was confirmed.

The present sample

t ^o C	Height of liquid rise (cm)	d ₁ ^t	γ (dyne/cm)	$\frac{M}{D-d} \cdot \gamma^{3/4}$
16.8	1.44	0.8998	28.76	396.8
29.9	1.40	0.8913	27.38	396.8
37.3	1.37	0.8854	26.62	395.6
46.9	1.34	0.8775	25.74	395.8
52.3	1.32	0.8740	25.32	395.7
Average				396.1
$\Sigma(P)$				381.4

r-Menthone

t°C	Height of liquid rise (cm)	d_4^t	γ (dyne/cm)	$\frac{M}{D-d} \gamma^{1/4}$
12.5	1.52	0.9041	30.16	399.7
26.2	1.47	0.8936	28.83	399.8
37.4	1.44	0.8854	27.96	400.6
Average				400.0
$\Sigma(P)$				405.1

	P. (observed)	P (calculated)	Δ
The present substance	396.1	381.9	+14.2
r-Menthone	400.0	405.1	- 5.1
Ethylene oxide ³⁶⁾	112.5	98.0	+14.5

Results of elementary analysis

Sample	CO ₂	H ₂ O	C%	H%
0.1074 gr.	0.3067 gr.	0.1165 gr.	77.88	12.14
0.1546	0.4402	0.1642	77.66	11.88
0.0984	0.2804	0.1065	77.72	12.11
Average			77.75	12.04
C ₁₀ H ₁₈ O			77.85	11.77

From these results the present substance obtained by the oxidation of menthene by peracids is presumed to be menthene oxide.

§ The formation of menthene glycol-3.4 from menthene oxide.

10 gr of menthene oxide with 10 times its volume of 10% sulphuric acid was agitated for a long while under ice-cooling until the oily layer of oxide floating on the aqueous solution disappeared. The viscous dense liquid precipitated on the bottom was repeatedly extracted with ether. From this extract, the solvent was expelled and the residual liquid was rectified under diminished pressure. The viscous liquid, boiling at (127-137)₁₄, was obtained with the yields of 13.4 gr. from which a solid matter, melting at 75°~76°, was crystallized out. This crystal was proved to be composed of menthene glycol-3.4 by its properties and also from the results of elementary analysis.

Sample	CO ₂	H ₂ O	C%	H%
0.1513 gr.	0.3847 gr.	0.1606 gr.	69.35	11.88
0.1104	0.2821	0.1163	69.70	11.79
Average			69.53	11.84
C ₁₀ H ₂₀ O ₂			69.77	11.63

§ The formation of i-menthone from menthene glycol-3,4.

With 5 times its volume of 10% sulphuric acid, menthene glycol was heated on a water-bath under vigorous stirring. At first the glycol was almost dissolved in the sulphuric acid forming an opalescent liquid, but by continuous heating, the solution became clear again with the separation of a fragrant liquid. The liquid thus obtained was rectified and from various properties as shown below was confirmed to consist of i-menthone :

Sample	Time for heating	Yield	B. p.	d_4^{25}	n_D^{25}	$(\alpha)_D$
I 10 gr.	2 hr	5.0 gr. (57.1%)	205°-209°	0.8943	1.4567	± 0
II 10	8	3.9 (44.6)	204°-209°	0.8959	1.4569	± 0

Sample	CO ₂	H ₂ O	C%	H%
I. { 0.1051 gr. 0.1842	0.3006 gr.	0.1128 gr.	78.01	12.01
	0.5265	0.1999	77.95	12.14
II. { 0.1145 0.1088	0.3265	0.1220	77.83	11.97
	0.3111	0.1167	77.99	12.00
Average			77.94	12.04
C ₁₀ H ₁₈ O			77.85	11.77

Oxime M. p. [79-80°]

Sample	N ₂	t°C	P	N%
3.804 mg	0.284 c.c.	18°	759 m.m.	8.58
7.158	0.525	17	759	8.49
Average				8.54
C ₁₀ H ₁₈ ON				8.28

Semicarbazone M. p. [209°]

Sample	N ₂	t°C	P	N%
5.879 mg	0.982 c.c.	19.5°	757 m.m.	19.09
4.283	0.752	18.5	757	20.14
Average				19.62
C ₁₁ H ₂₁ ON ₃				19.91

When menthene oxide was directly heated on a water-bath with 10% sulphuric acid, i-menthone was also produced with a very poor yield and the major part of oxide was found to be converted into resinous matter.

Sample	Time for heating	Yield	B. p.	d_4^{25}	n_D^{25}	$(\alpha)_D$
10 gr.	2 hr	2.3 gr. (26.3%)	203°-209°	0.8977	1.4535	± 0

Sample	CO ₂	H ₂ O	C%	H%
0.1993 gr.	0.5707 gr.	0.2103 gr.	78.10	11.81
0.2144	0.6124	0.2307	77.91	12.04
Average			78.01	11.93
C ₁₀ H ₁₈ O			77.85	11.77

§ The isomerization of menthene oxide by alumina.

24 gr. of menthene oxide were passed over a thin layer of alumina heated to 250° at the rate of 10 gr. per hour. The reaction product thus obtained was fractionated into the following three parts by distillation.

Fraction	B. p.	Yield
1	(62-74°) ₁₃	7.0 gr.
2	(80-95°) ₁₃	8.1
3	(95-) ₁₃	5.1

The first fraction was rectified with metallic sodium and was proved by its physical properties and also by the results

of analysis to consist of terpene hydrocarbon.

B. p. = 171-173°, $d_4^{25} = 0.8294$, $n_D^{25} = 1.4647$
 M. R. = 45.37, C₁₀H₁₆F₂ = 45.25

Sample	CO ₂	H ₂ O	C%	H%
0.1047 gr.	0.3715 gr.	0.1238 gr.	88.34	12.08
0.1046	0.3357	0.1134	87.53	12.13
Average			87.94	12.11
C ₁₀ H ₁₆			88.12	11.88

By its physical and chemical properties, and by the results of elementary analysis, the second fraction was also confirmed to be composed of i-menthone.

B. p. = 203~209°, $d_4^{25} = 0.9007$, $n_D^{25} = 1.4578$
 $(\alpha)_D = \pm 0$, M. R. = 46.69, C₁₀H₁₈O = 46.19
 Oxime M. p. (78-79°) Semicarbazone M. p. (207-208.5°)

Sample	CO ₂	H ₂ O	C%	H%
0.1028 gr.	0.2944 gr.	0.1087 gr.	78.11	11.83
0.0874	0.2501	0.0951	78.04	12.18
Average			78.08	12.01
C ₁₀ H ₁₈ O			77.85	11.77

§ The oxidation of menthene by hypochlorous acid.

30 gr. of menthene were suspended in 500 c.c. of the aqueous solution of sodium hypochlorite (available oxygen content 3.6 gr.). To this mixture, 200 c.c. of 2% zinc sulphate solution was added drop by drop with vigorous stirring. After the available oxygen in the mixture disappeared, the reaction products were extracted with ether and the solvent was distilled off.

The residue was composed of a very unstable compound which decomposed at once with the violent liberation of hydrogen chloride and water by distillation even at the pressure of 10 m.m. of mercury. Thus, 20 gr. of unrefined sample of the reaction product which had been extracted with ether, was dissolved in 100 c.c. of ether and twice that amount (calculated) of caustic potash powder was added under vigorous agitation until the ether solution showed no sign of positive reaction for halogen test. Then the solid matter was filtered off, and from the filtrate, the following four fractions were obtained by fractional distillation.

Fractions	B. p.	Yield	d_4^{25}	n_D^{25}	$[\alpha]_D$
1	(-78°) ₁₅	1.0 gr.			
2	(78-82°) ₁₅	4.0 (29.0%)	0.8903	1.4451	+25.85°
3	(82-100°) ₁₅	1.6			
4	(100°—) ₁₅	10.3			

The second fraction was proved by its properties and also by the results of analysis to consist of menthene oxide.

Sample	CO ₂	H ₂ O	C%	H%
0.1044 gr.	0.2974 gr.	0.1118 gr.	77.70	11.98
0.1157	0.3289	0.1241	77.54	12.00
Average			77.62	11.99
C ₁₀ H ₁₈ O			77.85	11.77

§ The oxidation of menthene by hypoiodous acid.

30 gr. of menthene were dissolved in 100 c.c. of ether and with 4 c.c. of water and 25 gr. of red mercuric oxide freshly prepared, the ether solution was stirred vigorously under cooling, after which 50 gr. of powdered iodine were dropped in a little at a time. When the total iodine was added and the colouration by iodine disappeared, the precipitate of mercuric iodide formed was filtered off and the ether solution was washed with a small volume of solution of sodium sulphite

and potassium iodide successively, to remove traces of iodine and mercuric iodide suspended. After distilling off the solvent, 51 gr. of the dense liquid was obtained. This was treated in the same way as when hypochlorous acid was used, with the following results :

Fraction	B. p.	Yield	d_4^{25}	n_D^{25}	$[\alpha]_D$
1	(-85°) ₁₉	3 gr.	0.8495	1.4479	
2	(85-100°) ₁₉	16 (65.1%)	0.8933	1.4490	+54.72°
3	(100-120°) ₁₉	4	0.9296	1.4562	+37.46
4	(120°-) ₁₉	8.5			

The second fraction was confirmed to consist of menthene oxide as follows :

$$\text{B. p.} = (92-98^\circ)_{20}, \quad d_4^{25} = 0.8965, \quad n_D^{25} = 1.4479 \quad [\alpha]_D = +51.96^\circ$$

Sample	CO ₂	H ₂ O	C%	H%
0.1114 gr.	0.3178 gr.	0.1184 gr.	77.80	11.89
0.1713	0.4873	0.1823	77.59	11.91
Average			77.70	11.90
C ₁₀ H ₁₈ O			77.85	11.77

§ The reaction between menthene iodohydrine and silver benzoate or silver acetate.

(I) 20 gr. of menthene iodohydrine prepared by the above method, was dissolved in 50 c.c. of 80% alcohol and heated on a water-bath with 12 gr. of silver benzoate for 5 hours. After the solid matter was filtered off from the mixture, the alcoholic solution was evaporated. The residual liquid was again dissolved in ether and shaken with 10% caustic soda solution to separate the acidic substance. The neutral substance thus obtained was rectified and 3.1 gr. (38.0%) of the liquid which was proved from the following data to be menthene oxide, was obtained.

$$\text{B. p.} = (90-94^\circ)_{30}, \quad d_4^{25} = 0.8994, \quad n_D^{25} = 1.4463,$$

Sample	CO ₂	H ₂ O	C%	H%
0.1443 gr.	0.4113 gr.	0.1532 gr.	77.74	11.88
C ₁₀ H ₁₈ O			77.85	11.77

The acidic substance liberated from caustic soda solution with dilute sulphuric acid was also confirmed from the physical and chemical properties to consist of benzoic acid.

Yield 2.6 gr. (46.5%) M. p. [119°-121°]

Sample	CO ₂	H ₂ O	C%	H%
0.1147 gr.	0.2890 gr.	0.0511 gr.	68.71	4.98
0.2033	0.5117	0.0932	68.64	5.13
Average			68.68	5.06
C ₇ H ₆ O ₂			68.85	4.92

(II) With the purpose of examining the formation of ester-like substance during the process of the above reaction, the filtrate from the reaction product between 20 gr. of menthene iodohydrine and 12 gr. of silver benzoate was saponified by heating with a small amount of alkali and the yields of menthene oxide and benzoic acid thus formed were compared with those in case (I). The results are shown in the following table. Little difference between the yields of the reaction products

	Yield	B. p.	M. p.	d_4^{25}	n_D^{25}
Menthene oxide	2.9 gr.	(71-80°) ₁₁	—	0.8997	1.4461
Benzoic acid	2.4 gr.	—	120-121°		

from these two kinds of treatment was noticed and no sign of the formation of stable ester appeared in the process of this reaction.

(III) In place of silver benzoate, 12 gr. of silver acetate and 20 gr. of menthene iodohydrine were heated together by the same treatment and the formation of 2.4 gr. (30.0%) of menthene oxide, boiling at (68-80°)₁₁, $d_4^{25}=0.9008$ and $n_D^{25}=1.4465$, and of 1.2 gr. (41.4%) of acetic acid measured by acidimetry were confirmed.

§ The oxidation of stilbene by peracetic acid.

(I) Into 150 c.c. of the ether solution which contained 10 gr. of stilbene,³⁷⁾ melting at 120-122°, a calculated amount of peracetic acid was dropped and left to stand for about 200 hours in the ice-box. After the active oxygen content in the solution was completely exhausted, the solution was washed several times with water and dilute caustic soda solution successively to remove acetic acid. The solvent was distilled off and

Sample	CO ₂	H ₂ O	C%	H%
0.1333 gr.	0.4184 gr.	0.0742 gr.	85.60	6.23
0.1946	0.6113	0.1073	85.68	6.17
Average			85.64	6.20
C ₁₄ H ₁₂ O			85.71	6.12

a yield of 22.3 gr. of white crystal, melting at 67–69°, was gained; this showed the melting point of 69–71° after repeated recrystallization and was presumed, after elementary analysis, to consist of stilbene- α -oxide.³⁹⁾

(II) Similar oxidation of 20 gr. samples of stilbene by peracetic acid were performed in chloroform solution. In these cases, the reaction was accomplished in 19–20 hours and the following results were obtained.

	Yield of oxide	M. p. of oxide
1	21.7 gr.	60–64°
2	22.0	59.5–64°
3	21.0	59.5–64°

The reaction products were mixed together and dissolved in a small volume of methyl alcohol. By fractional crystallization from this solution, 2.9 gr. of more soluble

oxide, melting at 38°–40°, were obtained. This crystal after referring to the literature and also by the results of elementary analysis was supposed to be composed of stilbene- β -oxide.³⁹⁾

Sample	CO ₂	H ₂ O	C%	H%
0.2003 gr.	0.6282 gr.	0.1122 gr.	85.54	6.27
C ₁₄ H ₁₂ O			85.71	6.12

§ The rate of decomposition of peracids and their salts and the rate of oxygen addition to menthene and aldehyde by them.

Each 1/10 gr. mol. of menthene and benzaldehyde, showing B. p. = (77–79°)₁₈, $d_4^{25} = 1.0409$ and $n_D^{25} = 1.5425$, was mixed with 10 c.c. of chloroform solution of peracids or the aqueous solution of their sodium salt. The mixture was left to stand at 30°C and the changes in the available oxygen content were estimated from time to time by iodometry. Under the same conditions, the rate of natural decomposition of peracids and their salts were investigated. The results are shown in the following table:

Perbenzoic acid. Initial available oxygen content 0.0564 gr. in 10 c.c. of chloroform solution.

Time	Sample	Without reagent	With menthene	With benzaldehyde
0 min.		0.0564 gr.	0.0564 gr.	0.0564 gr.
10		0.0564	0.0463	0.0219
30		0.0564	0.0363	0.0064
45		0.0563	0.0300	0.0048
60		0.0563	0.0277	0.0025
90		0.0562	0.0200	0.0023
120		0.0561	0.0116	0.0023
180		0.0561	0.0108	0.0023
240		0.0560	0.0088	0.0023

Sodium salt of perbenzoic acid. Initial available oxygen content 0.0228 gr. in 10 c.c. of the aqueous solution.

Time \ Sample	Without reagent	With menthene	With bonzaldehyde
0 min.	0.0228 gr.	0.0228 gr.	0.0228 gr.
5	0.0227	0.0227	0.0039
20	0.0221	0.0226	0.0019
30	0.0214	0.0214	0.0010
45	0.0197	0.0196	trace
60	0.0188	0.0184	
90	0.0140	0.0143	
120	0.0113	0.0114	
240	0.0092	0.0090	
450	0.0019	0.0018	

Peracetic acid. Initial available oxygen content 0.0259 gr. in 10 c.c. of chloroform solution.

Time \ Sample	Without reagent	With menthene	With benzaldehyde
0 min.	0.0259 gr.	0.0259 gr.	0.0259 gr.
5	0.0259	0.0010	0.0210
15	0.0259	trace	0.0170
30	0.0259		0.0133
45	0.0259		0.0094
60	0.0259		0.0066
90	0.0259		0.0037
135	0.0259		0.0012

§ The oxidation of aldehydes by peracids.

(I) The oxidation of benzaldehyde by peracetic acid.

Into 10% chloroform solution of the calculated amount of peracetic acid, 10 gr. of benzaldehyde were added drop by drop with vigorous agitation and left to stand for 2 days in the ice-box. After the solvent was distilled off, the residual solid was washed with a small volume of water and dried. The solid matter thus gained, melting at 119°–120.5°, was proved to consist of benzoic acid by showing no sign of melting point depression with pure benzoic acid crystal. The yield of the acid was 22.7 gr. for the theoretical amount of 23.0 gr.

(II) The oxidation of acetaldehyde by perbenzoic acid.

Into 200 c.c. of 10% chloroform solution of perbenzoic acid, 50 c.c. of chloroform solution, in which 11 gr. of acetaldehyde was contained, was dropped slowly and left to stand for 2 days in the ice-box. After

the disappearance of the available oxygen in the solution, the amount of acid produced was estimated by acidimetry and the formation of acetic acid by this reaction was proved by the occurrence of the white precipitate by mercurous nitrate solution.

	c.c. of N/10 KOH required to neutralize 1 c.c. of the solution		The yield of acetic acid
Before reaction	26.47	26.44	
After reaction	30.15	29.99	14.4 gr.
Theoretical amount			15.0

§ Comparative studies on the rate of oxidation of 2,6-dimethyl octene $\Delta 6$, p-menthen $\Delta 3$, styrene, oenanthol and benzaldehyde by peracetic acid.

(I) The preparation of the samples.

2,6-Dimethyl octene $\Delta 6$ was prepared by the catalytic dehydration of τ -tetrahydro linalool with alumina and showed the following properties:

B. p. = 160–161°, $d_4^{25} = 0.7450$ and $n_D^{25} = 1.4250$.

Styrene was prepared from phenylethyl alcohol by the action of alumina at 300°C and showed the properties of B. p. = 143–145°, $d_4^{25} = 0.8979$ and $n_D^{25} = 1.5378$.

The oenanthol used was the article of trade and showed the properties of B. p. = (55–57°)₁₇, $d_4^{25} = 0.8171$ and $n_D^{25} = 1.4160$ by rectification.

(II) The rate of addition of oxygen by peracetic acid.

To 50 c.c. of 1/2 N. chloroform solution of each sample, 10 c.c. of peracetic acid (available oxygen content 0.4256 gr. and 0.3924 gr.) was added at 0°C and at regular intervals, 1 c.c. of the solution was pipetted out and the amount of the residual active oxygen was estimated by iodometry and also the rate of addition of oxygen atom to each mol. of sample was calculated. The results were as follows:

2,6-Dimethyl octene $\Delta 6$ (3.5 gr of the sample was dissolved in 50 c.c. of chloroform)

Time	$\frac{N}{10}$ Na ₂ S ₂ O ₃ required for 1 c.c. of the soln.	The amount of available oxygen remaining in the soln.	Oxygen added	O/Mol.
0 min.	— c.c.	0.4254 gr.	0 gr.	0
5	0.30	0.0178	0.4076	1.02
10	0.15	0.0089	0.4165	1.04
15	0.10	0.0059	0.4195	1.05

p-Menthene $\Delta 3$ (3.4 gr. of the sample was dissolved in 50 c.c. of chloroform)

Time	$\frac{N}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ required for 1 c.c. of the soln.	The amount of available oxygen remaining in the soln.	Oxygen added	O/Mol.
0 min.	— c.c.	0.5085 gr.	0 gr.	0
5	6.28	0.3731	0.1334	0.33
10	5.86	0.3481	0.1604	0.40
15	5.65	0.3357	0.1728	0.43
31	5.20	0.3089	0.1996	0.50
45	4.88	0.2899	0.2186	0.55
60	4.61	0.2739	0.2346	0.59
120	3.95	0.2347	0.2738	0.68
182	3.70	0.2198	0.2887	0.72
240	3.50	0.2079	0.3006	0.75
350	3.41	0.2026	0.3059	0.77
474	3.30	0.1960	0.3125	0.78

Styrene (2.6 gr. of the sample was dissolved in 50 c.c. of chloroform)

Time	$\frac{N}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ required for 1 c.c. of the soln.	The amount of available oxygen remaining in the soln.	Oxygen added	O/Mol.
0 min.	— c.c.	0.4254 gr.	0 gr.	0
5	6.85	0.4006	0.0248	0.06
10	6.75	0.3947	0.0307	0.08
30	6.43	0.3761	0.0493	0.12
60	6.25	0.3655	0.0599	0.15
120	5.91	0.3457	0.0797	0.20
180	5.54	0.3240	0.1014	0.25
240	5.16	0.3018	0.1236	0.31
300	4.80	0.2807	0.1447	0.36
360	4.42	0.2585	0.1669	0.42
420	4.10	0.2398	0.1856	0.47
1230	2.32	0.1357	0.2897	0.72
1380	2.10	0.1228	0.3026	0.76

Oenanthol (2.85 gr. of the sample was dissolved in 50 c.c. of chloroform)

Time	$\frac{N}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ required for 1 c.c. of the soln.	The amount of available oxygen remaining in the soln.	Oxygen added	O/Mol.
0 min.	— c.c.	0.3759 gr.	0 gr.	0
15	4.78	0.3039	0.0720	0.18
30	4.30	0.2734	0.1025	0.26

60	4.01	0.2550	0.1209	0.30
120	3.71	0.2359	0.1400	0.35
195	3.70	0.2352	0.1407	0.35
240	3.60	0.2289	0.1470	0.37
300	3.50	0.2235	0.1524	0.38
360	—	—	—	—
420	3.39	0.2155	0.1604	0.40
480	3.39	0.2155	0.1604	0.40

Benzaldehyde (2.15 gr. of the sample was dissolved in 50 c.c. of chloroform)

Time	$\frac{N}{10}$ Na ₂ S ₂ O ₃ required for 1 c.c. of the soln.	The amount of available oxygen remaining in the soln.	Oxygen added	O/Mol.
0 min.	— c.c.	0.5085 gr.	0 gr.	0
15	4.02	0.5037	0.0048	0.01
30	3.99	0.5006	0.0079	0.02
60	3.87	0.4849	0.0236	0.06
90	3.81	0.4774	0.0310	0.08
120	3.73	0.4690	0.0404	0.10
180	3.61	0.4524	0.0561	0.14
240	3.56	0.4461	0.0624	0.16
300	—	—	—	—
360	3.35	0.4198	0.0887	0.22
420	3.26	0.4085	0.1000	0.25
480	3.20	0.4010	0.1075	0.27
540	3.11	0.3897	0.1193	0.30
720	2.99	0.3747	0.1343	0.34

§ The autooxidation of benzaldehyde.

5 gr. of benzaldehyde and 10 c.c. of the chloroform solution of the oxidizing agents were placed in a flask of 90 c.c. capacity with a mercury manometer, and left to stand at 30°C. At definite intervals, the pressure decrease caused by the autooxidation of the aldehyde and also the amount of benzoic acid formed were measured. The results are shown in the following tables: Each result shows the average value of ten examinations.

Perbenzoic acid (available oxygen content 0.0151 gr.)

Time	Pressure decrease on manometer	Calculated amount of ben- zoic acid corresponding to oxygen consumed	Observed amount of benzoic acid
5 min.	8 m.m.	gr.	gr.
10	19		
15	31		

30	61		
45	78		
60	87	0.0710	0.1868
90	98		
120	107		
150	113		
180	119	0.1051	0.2168
240	123		
300	133	0.1137	0.2239
420	148	0.1257	0.2433
1200	148	0.1257	0.2437

The sodium salt of perbenzoic acid. (available oxygen content 0.0301 gr.)

Time	Pressure decrease	Calculated amount of benzoic acid corresponding to oxygen consumed	Observed amount of benzoic acid
5 min.	32 m.m.	gr.	gr.
10	44		
15	72		
30	104	0.0889	0.3138
45	115		
60	120	0.1026	0.3491
90	130		
120	142		
180	157	0.1240	0.3720
240	168		
300	173	0.1479	0.3973
420	183	0.1564	0.4126
1320	198	0.1693	0.4189

Peracetic acid (available oxygen content 0.0386 gr.)

Time	Pressure decrease	Calculated amount of benzoic acid corresponding to oxygen consumed	Observed amount of benzoic acid.
5 min.	6 m.m.	gr.	gr.
15	8		
30	11	0.0094	0.1808
45	15		
60	21	0.0180	0.2305
90	32		
120	42	0.0359	0.2609
150	56		
180	65	0.0556	0.3298
300	104	0.0889	0.3841
480	134	0.1146	0.4095

Menthene ozonide (available oxygen content 0.0138 gr.)

Time	Pressure decrease	Calculated amount of benzoic acid corresponding to oxygen consumed	Observed amount of benzoic acid
5 min.	42 m.m.	gr.	gr.
10	53		
15	65		
20	71		
30	81		
45	91		
50	103	0.0873	0.0953
90	116		
120	123		
180	127	0.1095	0.1423
240	127		
300	127	0.1095	0.1694
360	127		
420	127	0.1095	0.1868
540	127	0.1095	0.1893

§ The polymerization of menthene oxide.

With a drop of acetic acid, 20 gr. of menthene oxide were heated at 100° to 120°C for 20 minutes under the reflux condenser. The pale yellowish liquid was fractionated into the following two fractions by distillation :

Fraction	Yield	B. p.	d_4^{25}	n_D^{25}
1	14.7 gr. (75%)	(77-79°) ₁₄	0.9001	1.4461
2	4.9 (25%)	—		

The first fraction was confirmed by its properties to consist of unchanged menthene oxide. The second fraction was composed of very viscous liquid and not yet distilled even under high vacuum. The results of elementary analysis are as shown below in coincidence with the polymer of menthene oxide.

Sample	CO ₂	H ₂ O	C%	H%
0.1140 gr.	0.3260 gr.	0.1206 gr.	77.99	11.84
0.1025	0.2930	0.1074	78.04	11.74
Average (C ₁₀ H ₁₈ O) _n			78.02	11.79
			77.85	11.77

In conclusion, the writer wishes to express his sincere thanks to Prof. Dr. S. Komatsu for his kind guidance and valuable suggestions throughout his work and at the same time to the Department of Education for a research grant.

April, 1932,

Laboratory of Biochemistry,
Kyoto Imperial University.

Literature cited

- 1) O. Wallach, *Ann.*, **362**, 272 (1908).
R. Pickard & W. Littleberg, *J. C. S.* **101**, 112 (1912).
- 2) G. Wagner, *Ber.* **27**, 1639 (1894).
- 3) N. Prileschajew, *Ibid.*, **42**, 4811 (1909).
43, 959 (1910).
- 4) L. Brunel, *C. R.* **135**, 1055 (1902).
- 5) *Ber.*, **34**, 743 (1901).
- 6) O. Wallach, *loc. cit.*
R. Pickard & W. Littleberg, *loc. cit.*
- 7) W. Atkinson & H. Yoshida, *J. C. S.* **41**, 50 (1882).
E. Beckmann, *Ann.* **250**, 325 (1889).
H. Grossmann & K. Brauer, *J. pr. Chem.* [2] **98**, 49 (1918).
S. Komatsu & M. Kurata, *Memoir Sci. Kyoto Imp. Univ.* **9**, 23 (1925).
- 8) H. Limpricht & H. Schwanert, *Ann.*, **145**, 336 (1868).
153, 120 (1870).
J. Wislicenus & F. Seeler, *Ber.*, **28**, 2693 (1895).
- 9) S. Katô, *Bull. Inst. Phys. & Chem. Research* **11**, 765 (1932).
- 10) S. Sugden, "The Parachor and Valency" **38** (1930)
- 11) F. Eisenrohr, *Z. physik. Chem.* **75**, 585 (1910).
- 12) F. Kohlraush, "Die Smekal-Raman Effekt" **154** (1931).
- 13) S. Kimura, unpublished.
- 14) *C. R.* **124**, 951 (1897).
- 15) *Ber.* **30**, 1669 (1897).
- 16) *Ibid.*, **46**, 3530 (1913).
- 17) *Ann.*, **486**, 226 (1931).
- 18) *Rec. Trav. Chim.* **47**, 286 (1928).
- 19) *J. chim. phys.* **28**, 316 (1931).
- 20) *loc. cit.*
- 21) A. Bach & R. Chodat, *Bioch. Z.* **1**, 12 (1903).
Ber. **35**, 1275, 2466 (1902).
36, 606, (1903).
37, 1342 (1904).
M. Onslow, *Bioch. J.* **13**, 1 (1919).
14, 535 (1920).

- 22) R. Willstätter, *Ann.*, **416**, 21 (1918).
O. Warburg, *Z. f. physiol. Chem.* **92**, 231 (1914).
C. Enger & Weissberg, *Kritische Studien über die Vorgänge der Autoxydation.*
 - 23) A. Bach & R. Chodat, *loc. cit.*
B. Moore & E. Whitley, *Bioch. J.* **4**, 136 (1909).
M. Onslow, *Ibid.*, **13**, 1 (1913).
14, 535 (1920).
R. Willstätter, *loc. cit.*
O. Warburg, *loc. cit.*
 - 24) P. Gallagher, *Bioch. J.* **18**, 29 (1924).
 - 25) *Ann.*, **343**, 352 (1906).
 - 26) F. Fischer, *Ibid.*, **486**, 80 (1931).
 - 27) M. Bergmann, *Ber.*, **57**, 753 (1924).
Ann., **448**, 48 (1926).
Ber., **62**, 2297 (1929).
Ibid., **63**, 1911 (1930).
 - 28) J. Böeseken, *Rec. Trav. Chim.* **50**, 1823 (1931).
 - 29) A. Pictet, *Helv.* **1**, 37 (1918).
C. Tanaka, *Memoir Sci. Kyoto Imp. Univ.* **13**, 239 (1930).
 - 30) S. Komatsu, S. Tanaka & T. Waida, *J. C. S. Jap.* **54**, 794 (1933).
 - 31) *Bull. Soc. chim.* [4] **37**, 1597 (1925).
 - 32) *J. prak. Chem.* [2] **127**, 92 (1930).
 - 33) F. Eisenrohr, "Der molekular Brechungskoeffizient in der Reihe der Polymethylen Verbindungen."
 - 34) J. Thomson, "Thermochemistry" 371, 442.
 - 35) *Ibid.*, 373, 443.
 - 36) S. Sugden & H. Wilkins, *J. C. S.* 139 (1927).
 - 37) C. Hell, *Ber.*, **37**, 455 (1904).
 - 38) J. Böeseken & G. Schneider, *J. prak. Chem.* [2], **131**, 285 (1931).
 - 39) J. Böeseken & G. Schneider, *loc. cit.*
-