Studies on Styrene Ozonide.

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The writer's interest in the studies of ozone(1) particularly with respect to its preparation and its solubility in various solvents was directed by the suggestion of Prof. Komatsu toward the elucidation of the chemical state of ozonides which so far had not been definitely established.

As the first step the styrene ozonide has been studied. It has been found that this compound usually exists as polymers which will be described in the experimental part.

Experimental and Discussion.

I. Preparation of Styrene Ozonide. Purified styrene is dissolved in carbon tetrachloride, in benzene, in chloroform, or in ethyl ether. On cooling the above solutions in ice water about 2% ozonized air which has been washed with 5% potassium hydroxide solution is then passed through the solution at the speed of about 20 liter per hour. Immediately after the reaction is over petroleum ether is added to the reaction mixture and the styrene ozonide precipitate thus formed is filtered off. 20 g. of the dried ozonide precipitate is dissolved in 50 c.c. purified benzene. In case of ozonide prepared in carbon tetrachloride or in benzene, petroleum ether is added 3 times to the benzene solution using 5 c.c. at each time and shaking the solutions vigorously after each addition. Ozonide precipitate thus formed is indicated as Fraction A (F_A).

With the ozonide prepared in chloroform, its benzene solution is treated 6 times with petroleum ether using 5 c.c. at each time. The precipitate thus formed is indicated also as Fraction A (F_A). With ozonide prepared in ethyl ether its benzene solution is treated 16 times with petroleum ether using 5 c.c. at each time. The precipitate thus formed is indicated also as Fraction A (F_A).

To each mother liquor from which F_A has been separated is now added 5 c.c. petroleum ether and the precipitate formed is collected, thus repeating the same procedure until no more precipitate comes out. The precipitates obtained by this series of treatment are united and indicated as Fraction B (F_B). F_A and F_B are dried in a desiccator under reduced pressure, 5–6 mm. Hg.

All these precipitates have been subjected to the elementary analyses, the results of which are indicated in Table 1. It shows that all these ozonide precipitates have the same elementary composition within the limits of the experimental errors.

During the above experiment it has been found that these ozonide

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(1) F. Kawamura, *J. Chem. Soc. Japan*, **53** (1932), 783; **54** (1933), 553; **55** (1934), 849.

Table 1. Results of Elementary Analysis of Styrene Ozonide Preparations.

Solvent	Yield		Material used	C	H
	Fraction	(%)	(mg.)	(%)	(%)
Carbon tetrachloride	A	62	1.375	63.91	5.32
	B	32	1.459	63.06	5.25
Benzene	A	66	1.520	64.01	5.33
	B	21	1.432	63.11	5.31
Chloroform	A	56	1.601	63.95	5.29
	B	32	1.386	63.17	5.23
Ethyl ether	A	45	1.474	63.65	5.32
	B	39	1.542	63.03	5.23
	Calcd. for $C_8H_8O_3$			63.15	5.30

preparations decompose on being brought to contact with moisture into benzaldehyde, benzoic acid, formaldehyde, formic acid and hydrogen peroxide.

II. Effect of Styrene Ozonide upon Styrene Polymerization. During the ozonization it has been found that a part of styrene undergoes polymerization to produce a resinous substance, thus the yield of styrene ozonide being much reduced. With the purpose of finding out the cause of this styrene polymerization the reaction between monostyrene and styrene ozonide has been investigated by the methods described below. It has, thus, been found that the latter possesses no oxidative action upon the former but accelerates markedly the polymerization of the former.

a) *Effect of Styrene Ozonide Concentration.* To styrene is added the ozonide prepared in chloroform as indicated in Section I at the concentrations of 0, 0.04, 0.20, and 0.72 mole per liter, and the mixture is put in the Ostwald viscosimeter immersed in a thermostat at 40° and 50°. Its viscosity is measured at various intervals of time, from which the velocity of polymerization has been determined. The results are indicated in Figure 1. It shows that the ozonide promotes the polymerization, the effect of the ozonide concentration being marked when its concentration is small but becoming less marked as it increases.

For instance, the viscosity attained in 144 hours at 50° by styrene to which no ozonide has been added is attained in 42, 24, and 18 hours by those containing respectively 0.04, 0.2, and 0.72 mole per liter ozonide. This is in accord with the results obtained by Hantz and Adkins(2) for styrene polymerization by di-isobutylene ozonide.

Figure 1 also shows that the reaction consists of two stages, Induction and Polymerization Stages. It is of interest to note that the increase in

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(2) Hantz and Adkins, *J. Am. Chem. Soc.*, **53** (1931), 1058; **55** (1933), 1609.

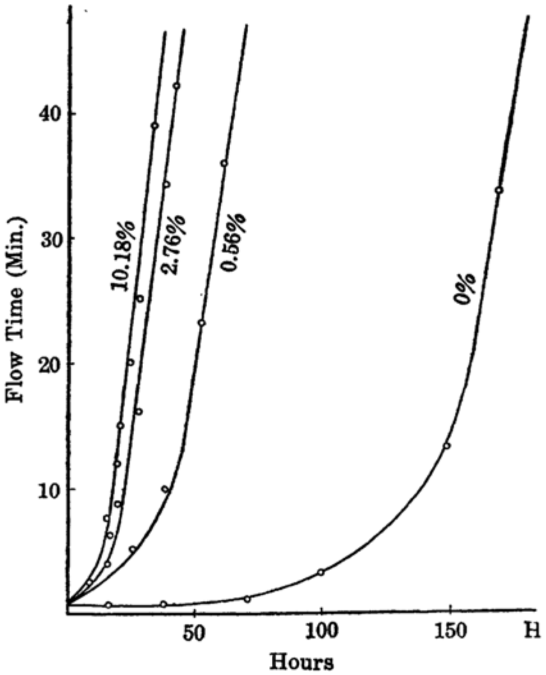


Fig. 1. Effect of Styrene Ozonide Concentration upon the Styrene Polymerization.

styrene ozonide concentration shortens the induction period, but has no effect upon the rate of polymerization.

b) *Effect of Temperature.* The styrene polymerization in the presence of varying amount of styrene ozonide has been studied at 30°, 40° and 50°, the results of which are plotted in Figure 2. It is seen from this figure that at 30° styrene containing 0.20 mole per liter of the ozonide attains a certain viscosity after 288 hours while at 40° the same viscosity is attained after 72 hours, and at 50° after 28 hours. Thus, the polymerization by the action of the ozonide is accelerated by the temperature rise. Like the effect of the concentration the temperature effect is also for the shortening of the induction period but not for the polymerization period. Figure 2 also shows that the lower the temperature, the more marked the effect of styrene ozonide concentration.

c) *Effect of the Decomposition Products.* As has been previously stated styrene ozonide decomposes by the action of water to benzaldehyde, formaldehyde, benzoic acid, and formic acid, also often this ozonide is mixed with some polystyrene. The effect of these decomposition products upon the styrene polymerization has, therefore, been investigated. That is, the velocity of the polymerization has been measured with pure styrene to which 0.20 mole per liter of each of these substances has been added separately. It has thus been found that benzaldehyde and polystyrene accelerate the polymerization although their effect is slight in comparison with that of styrene ozonide, whereas benzoic acid, formic acid, and formaldehyde retard the polymerization.

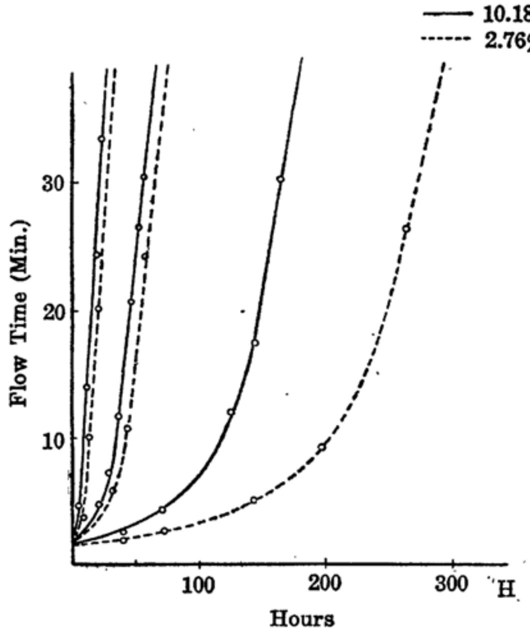


Fig. 2. Effect of Temperature upon the Styrene Polymerization.

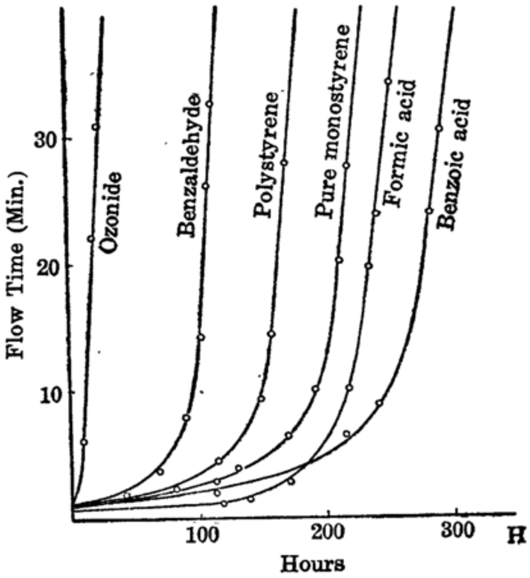
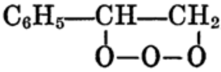
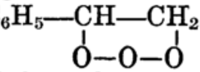
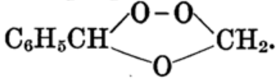


Fig. 3. Effect upon the Styrene Polymerization of the Decomposition Products of Styrene Ozonide, Benzaldehyde, Formaldehyde, Benzoic Acid, Formic Acid, and Polystyrene.

III. Polymerization of Styrene Ozonide. It has been stated in section I that styrene ozonide is prepared in various solvents. These ozonide preparations have been found to possess different viscosities. This is probably due to the fact that the ozonide is not a simple molecule as indicated by the formula,  $\begin{array}{l}C_6H_5-CH-CH_2\\ \qquad\quad\;\, | \qquad |\\ \qquad\quad\;\, O-O-O\end{array}$, but its polymers at different polymerization stages.

According to Harries$^{(3)}$, Fonrobert$^{(4)}$, and Wagner$^{(5)}$ the molecular structure of styrene ozonide is of glycol type, i.e.  $\begin{array}{l}C_6H_5-CH-CH_2\\ \qquad\quad\;\, | \qquad |\\ \qquad\quad\;\, O-O-O\end{array}$. The production of benzaldehyde, hydrogen peroxide, and formaldehyde in the reaciton of the ozonide and water supports this view. On the other hand, Baeyer$^{(6)}$ Staudinger$^{(7)}$, Rieche$^{(8)}$ and Pummerer$^{(9)}$ have proposed as the results of their studies the formula of acetal type, i.e.  $C_6H_5CH\begin{array}{c}O-O\\ O\end{array}CH_2$. In fact, no glycol derivative is formed by the reduction of the ozonide.

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(3) Harries, "Untersuchungen über Ozon und seine Einwirkung auf Organische Verbindungen," 48 (1916); *Ann.*, **410** (1915), 29.
(4) Fonrobert, "Das Ozon," 135 (1916).
(5) Wagner, *Ann.*, **410** (1915), 29.
(6) Baeyer and Villiger, *Ber.*, **32** (1899), 3625; **33** (1900), 858.
(7) Staudinger, *Ber.*, **58** (1925), 1088.
(8) Rieche, "Alkylperoxyd und Ozonid," (1913).
Z. angew. Chem., **43** (1930), 628; **44** (1931), 590; **45** (1932), 441.
Ber., **63** (1930), 2647.
(9) Pummerer, *Ann.*, **529** (1939), 33.
Z. angew. Chem., **47** (1934), 366.

However, the ozonide prepared at the present experiment is a highly viscous liquid of resinous consistency. Furthermore, the ozonide, like peroxides, induces polymerization for styrene but unlike the latter exerts no oxidizing action.

These chemical properties also support the view that the ozonide exists in polymerized form. It is then expected that the stage of polymerization, that is the number of monomer polymerized, depends upon the nature of the solvent used, particularly upon its dipole moment. With the purpose of confirming this view the benzene solutions of the ozonides prepared in the different solvents as mentioned in Section I, have been examined with respect to the viscosity and the freezing point.

The results have shown that they are in fact polymers and also that there is parallelism between the dipole moment of the solvent used for its preparation and the stage of the ozonide polymerization, e.g. the lower the dipole moment is, the higher the polymerization stage.

a) *Molecular Weight Determination by Cryoscopic Method.* As described in Section I styrene ozonide has been freshly prepared using the 4 different solvents and its benzene solution has been subjected to the determination of freezing point by the ordinary method and average molecular weight has been calculated from the results. They are shown in Table 2.

It is seen from the table that F_A and F_B of carbon tetrachloride, $\mu=0$, have different average molecular weight. That of the former, 882, may be approximated to 912, indicating the formula, $(C_8H_8O_3)_6$. That of the latter, 678, is roughly equal to 608 which corresponds to the composition,

Table 2. Molecular Weight of Styrene Ozonide by Cryoscopic Method.

a) Ozonide prepared in Carbon Tetrachloride; $\mu = 0$.

Fraction		Yield		Amount of material used	Δt	Mol. Wt.	Formula
		g.	%	g.	°C.		
F_A	1	3.85	56	0.4435	0.140	896	$\simeq 912 = (C_8H_8O_3)_6$
	2	3.83		0.4264	0.108	884	
	3	3.64		0.4536	0.117	865	
F_B	4	3.36	33	0.4665	0.112	692	$\simeq 608 = (C_8H_8O_3)_4$
	5	3.33		0.4732	0.155	662	
Total amount used		20.30		0.4643	0.159	725	
Loss		2.30	11				

Fraction 1(F_1) has been precipitated by adding to 50 c.c. benzene solution 5 c.c. petroleum ether.
Fraction 2(F_2) Mother liquor of F_1 + 5 c.c. petroleum ether.
Fraction 3(F_3) ,, ,, ,, F_2 + 5 c.c. ,, ,,
Fraction 4(F_4) ,, ,, ,, F_3 + 10 c.c. ,, ,,
Fraction 5(F_5) ,, ,, ,, F_4 + 15 c.c. ,, ,,

$(C_8H_8O_3)_4$. Thus, styrene ozonide prepared in carbon tetrachloride, may be considered to consist of 56% $(C_8H_8O_3)_6$ and 33% $(C_8H_8O_3)_4$.

Similarly the ozonide prepared in benzene, $\mu=0$, consists of 56% hexamer (in F_A) and 29% tetramer (in F_B). The ozonide prepared in chloroform, $\mu=0.95\times10^{-18}$, contains 57% tetramer (in F_A) and 25% dimer (in F_B), but no hexamer. With the ozonide prepared in ethyl ether, $\mu=1.10\times10^{-18}$, 78% dimer only has been found. All these results are recorded in Table 2.

b) Ozonide prepared in Benzene, $\mu = 0$.

Fraction	Yield		Amount of material used	Δt	Mol. Wt.	Formula
	g.	%	g.	°C.		
F_A 1	4.13	59	0.3146	0.082	876	$\simeq 912 = (C_8H_8O_3)_6$
2	3.88		0.3364	0.089	858	
3	3.65		0.3483	0.095	832	
F_B 4	2.95	29	0.3567	0.121	672	$\simeq 608 = (C_8H_8O_3)_4$
5	2.88		0.3725	0.132	644	
Total amount used	19.95		0.3426	0.109	715	
Loss	2.55	13				

Fractions 1, 2, 3, 4, and 5 have been obtained from benzene solution exactly in the same way as in Table 2a.

c) Ozonide prepared in Chloroform, $\mu = 0.95 \times 10^{-18}$.

Fraction	Yield		Amount of material used	Δt	Mol. Wt.	Formla
	g.	%	g.	°C.		
F_A 1	4.12	57	0.3435	0.133	585	$\simeq 608 = (C_8H_8O_3)_4$
2	3.84		0.3628	0.146	569	
3	3.82		0.3766	0.155	554	
F_B 4	3.66	35	0.3845	0.226	388	$\simeq 304 = (C_8H_8O_3)_2$
5	3.61		0.3850	0.253	346	
Total amount used	20.50		0.3762	0.176	486	
Loss	1.45	7				

Fraction 1 (F_1) has been precipitated by adding to 50 c.c. benzene solution 10 c.c. petroleum ether.
Fraction 2 (F_2) Mother liquor of F_1 + 10 c.c. petroleum ether.
Fraction 3 (F_3) " " " F_2 + 10 c.c. " "
Fraction 4 (F_4) " " " F_3 + 20 c.c. " "
Fraction 5 (F_5) " " " F_4 + 20 c.c. " "

d) Ozonide prepared in Ethyl Ether, $\mu = 1.10 \times 10^{-18}$.

Fraction		Yield		Amount of material used	Δt	Mol. Wt.	Formula
		g.	%	g.	°C.		
F_A	1	3.16	76	0.3674	0.290	288	$\simeq 304 = (C_8H_8O_3)_2$
	2	3.28		0.3752	0.322	265	
	3	3.45		0.3566	0.320	254	
	4	3.06		0.3622	0.330	250	
	5	2.37		0.3455	0.325	242	
Total amount used		20.75		0.3865	0.341	289	
Loss		5.43	27				

Fraction 1(F_1) has been precipitated by adding to 50 c.c. benzene solution 50 c.c. petroleum ether.
Fraction 2(F_2) Mother liquor of F_1 + 15 c.c. petroleum ether.
Fraction 3(F_3) ,, ,, ,, F_2 + 15 c.c. ,, ,,
Fraction 4(F_4) ,, ,, ,, F_3 + 30 c.c. ,, ,,
Fraction 5(F_5) ,, ,, ,, F_4 + 40 c.c. ,, ,,

b) *Molecular Weight Determination by Viscosity Measurement.* According to Staudinger⁽¹⁰⁾ molecular weight of a substance in colloidal solution, e. g. styrene ozonide in benzene, can be determined by viscosity measurement more accurately than by the freezing point method. With benzene solution of each fraction of the ozonide prepared in the previous experiment relative viscosity has been measured at 20° by means of the Ostwald viscosimeter. From this value the molecular weight as well as the number of monomer polymerized has been calculated according to the Staudinger equations:

$$\eta_{sp} / C_{gm} = K_m \cdot M \,\ldots\ldots.\, (1) \qquad \eta_{sp} / C = K_m \cdot n \,\ldots\ldots.\, (2)$$

where η_{sp}, M, n, C_{gm} and C are respectively relative viscosity, molecular weight, number of monomer constituting a polymer, molar concentration, and concentration in grams per liter. Km is viscosity-molecular weight constant and its value is taken as 8.3×10^{-4}.

The results thus obtained with the ozonide prepared in carbon tetrachloride, benzene, chloroform, and ethyl ether are shown in Table 3. It shows that the ozonide prepared in carbon tetrachloride contains 55% hexamer (F_A) and 34% tetramer (F_B).

The ozonide prepared in benzene contains 56% hexamer and 23% tetramer. This result is also in agreement with that obtained by freezing point method (Table 2) as well as with that of ozonide prepared in carbon tetrachloride. The ozonide prepared in chloroform contains 56% tetramer and 31% dimer, but no hexamer. In F_A and F_B from ethyl ether only dimer has been found by this method. All these results are in agreement with those obtained by the freezing point method which are shown in Table 2.

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(10) Staudinger, *Z. angew. Chem.*, **49** (1936), 574.

Table 3. Molecular Weight of Styrene Ozonide by Viscosity Method.

a) Ozonide prepared in Carbon Tetrachloride

i. Molecular Weight

(calculated according to $\eta_{sp}/C_{gm} = K_m \cdot M \quad K_m = 8.3 \times 10^{-4}$)

Fraction	Yield g.	Yield %	η_{sp}	C_{gm}	Mol. Wt. from η_{sp}	Mol. Wt. from F.P.	Formula
F_A 1	4.35	55	0.23	0.325	862 ≃	875	≃ 912 = $(C_8H_8O_3)_6$
F_A 2	5.38		0.21	0.298	855 ≃	860	
F_B 3	6.39	34	0.16	0.301	640 ≃	652	≃ 608 = $(C_8H_8O_3)_4$
Material used	18.85		0.21	0.300	850	855	
Loss	2.16	11					

ii. Number of Monomer polymerized

(calculated according to $\eta_{sp}/C = K_m \cdot n$)

Fraction	C	η_{sp}/C	n
F_A 1	49.4	46.6×10^{-4}	5.6 ≃ 6
F_A 2	45.3	46.3× ,,	5.6
F_B 3	45.7	35.0× ,,	4.2 ≃ 2
Total mixture	45.7	46.0× ,,	5.6

F_1 has been precipitated by adding to 50 c.c. benzene solution 5 c.c. petroleum ether.
F_2, Mother liquor of F_1 + 10 c.c. petroleum ether.
F_3, ,, ,, ,, F_2 + 25 c.c. ,, ,,

b) Ozonide prepared in Benzene.

i. Molecular Weight

Fraction	Yield g.	Yield %	η_{sp}	C_{gm}	Mol. Wt. from η_{sp}	Mol. Wt. from F.P.	Formula
F_A 1	5.38	65	0.23	0.322	850 ≃	865	≃ 912 = $(C_8H_8O_3)_6$
F_A 2	7.27		0.21	0.301	830 ≃	829	
F_B 3	4.63	23	0.15	0.300	600 ≃	658	≃ 608 = $(C_8H_8O_3)_4$
Material used	19.50		0.19	0.275	825	805	
Loss	2.22	11					

ii. Number of Monomer polymerized

Fraction		C	η_{sp}/C	n
F_A	1	49.0	46.9×10^{-4}	5.1 } ≃ 6
	2	45.9	$45.9\times$,,	5.5
F_B	3	45.0	$33.3\times$,,	4.0 ≃ 4
Total mixture		41.7	$41.6\times$,,	5.5

F_1 has been precipitated by adding to 50 c.c. benzene solution 5 c.c. petroleum ether.
F_2, Mother liquor of F_1 + 10 c.c. petroleum ether.
F_3, ,, ,, ,, F_2 + 25 c.c. ,, ,,

c) Ozonide prepared in Chloroform.

i. Molecular Weight

Fraction		Yield		η_{sp}	C_{gm}	Mol. Wt. from η_{sp}	Mol. Wt. from F.P.	Formula
		g.	%					
F_A	1	5.59	56	0.20	0.471	580 ≃	564	≃ 608 = $(C_8H_8O_3)_4$
	2	5.93		0.18	0.390	565 ≃	543	
F_B	3	6.19	31	0.11	0.387	333 ≃	364	≃ 304 = $(C_8H_8O_3)_2$
Material used		20.10		0.13	0.280	560	505	
Loss		2.39	12					

ii. Number of Monomer polymerized

Fraction		C	η_{sp}/C	n
F_A	1	63.4	31.6×10^{-4}	3.8 } ≃ 4
	2	59.4	$30.3\times$,,	3.7
F_B	3	58.8	$18.7\times$,,	2.3 ≃ 2
Total mixture		42.6	$30.5\times$,,	3.6

F_1 has been precipitated by adding to 50 c.c. benzene solution 15 c.c. petroleum ether.
F_2, Mother liquor of F_1 + 15 c.c. petroleum ether.
F_3, ,, ,, ,, F_2 + 40 c.c. ,, ,,

d) Ozonide prepared in Ethyl Ether.

i. Molecular Weight

Fraction	Yield		η_{sp}	C_{gm}	Mol. Wt. from η_{sp}	Mol. Wt. from F.P.	Formula
	g.	%					
F_A 1	5.68	78	0.14	0.566	300 ≃	280	≃ 304 = $(C_8H_8O_3)_2$
F_A 2	4.88		0.13	0.565	277 ≃	264	
F_A 3	4.84		0.13	0.560	258 ≃	250	
Material used	19.78		0.13	0.505	285	298	
Loss	4.38	22					

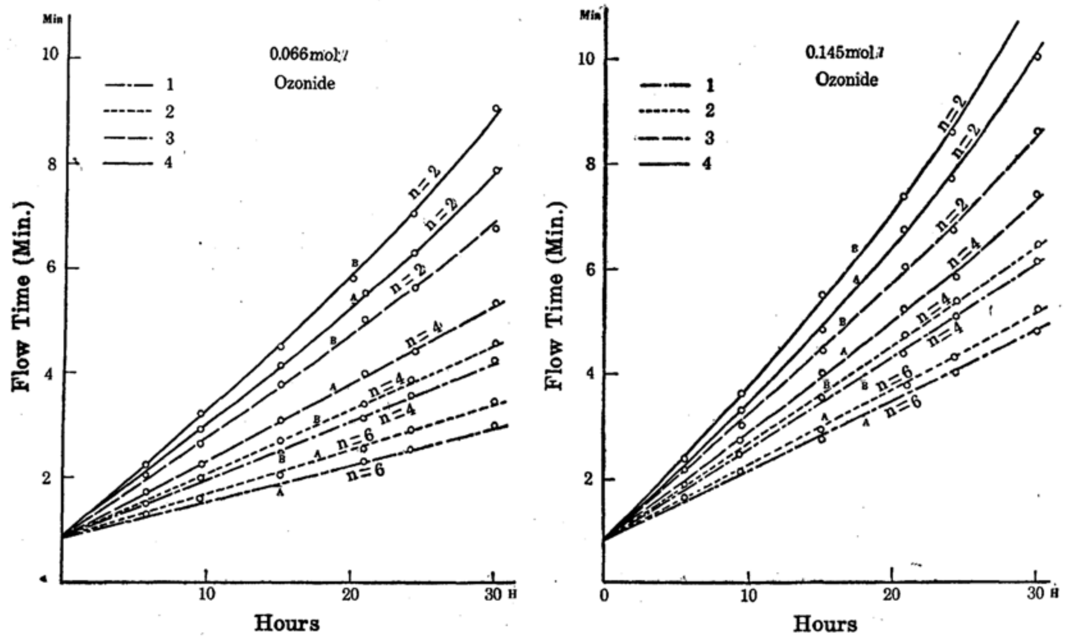
ii. Number of Monomer polymerized

Fraction	C	η_{sp}/C	n
F_A 1	86.0	16.3×10^{-4}	2.0 ≃ 2
F_A 2	85.8	$15.3\times$,,	1.8
F_A 3	85.2	$14.1\times$,,	1.7
Total mixture	76.7	$16.9\times$,,	2.2

F_1 has been precipitated by adding to 50 c.c. benzene solution 65 c.c. petroleum ether.
F_2, Mother liquor of F_1 + 25 c.c. petroleum ether.
F_3, ,, ,, ,, F_2 + 70 c.c. ,, ,,

IV. Reactivity of Styrene Ozonide. As has been stated in Section II, styrene ozonide does not oxidise styrene but induces its polymerization. This fact may also be considered as supporting the conclusion of the previous experiments that the ozonide is a mixture of polymers. In order to see whether or not the reactivity of the polymers varies with the number of monomers polymerized the following experiments have been carried out.

a) *Promotion of Styrene Polymerization.* Each fraction of the ozonide obtained by fractional precipitation as described in Section I has been added to styrene so that the ozonide concentration may be 0.066 and 0.145 mole per liter (calculated as monomer). This mixture is put in the Ostwald viscosimeter immersed in a thermostat at 50°, and the viscosity is measured at various intervals of time. The results are shown in Table 4 and also in Figures 4 and 5. They indicate distinctly that each ozonide preparation accerelates the polymerization to different degree. Namely F_A of carbon tetrachloride and of benzene, both of which consist of the highest polymer, hexamer, as shown in Tables 4 a and b, accelerates the polymerization to the least extent, whereas F_B of chloroform and F_A and F_B of ethyl ether, all of which consist of the dimer, accelerate it to the



1. Ozonide prepared in carbon tetrachloride.
2. Ozonide prepared in benzene.
3. Ozonide prepared in chloroform.
4. Ozonide prepared in ethyl ether.

A. Fraction A (F_A).
B. Fraction B (F_B).

Figs. 4 and 5. Acceleration of Styrene Polimerization by Styrene Ozonide.

Table 4. Acceleration of Styrene Polymerisation by Styrene Ozonide observed through Viscosity Change.

a) Ozonide prepared in Carbon Tetrachloride.

Time elapsed (hrs.)	Flow Time (min. : sec.)					
	Total ozonide		F_A (hexamer)		F_B (tetramer)	
	0.066 M	0.145 M	0.066 M	0.145 M	0.066 M	0.145 M
0	0 : 54	0 : 56	0 : 54	0 : 56	0 : 54	0 : 56
3	1 : 11	1 : 15	1 : 06	1 : 13	1 : 12	1 : 22
6	1 : 28	1 : 38	1 : 17	1 : 34	1 : 38	1 : 54
9	1 : 40	2 : 03	1 : 30	1 : 48	2 : 03	2 : 23
12	1 : 56	2 : 26	1 : 41	2 : 14	2 : 26	2 : 56
15	2 : 18	2 : 50	1 : 54	2 : 36	2 : 50	3 : 27
21	2 : 45	3 : 31	2 : 21	3 : 18	3 : 38	4 : 23
24	3 : 10	3 : 56	2 : 37	3 : 35	4 : 06	4 : 58
27	3 : 24	4 : 22	2 : 46	3 : 54	4 : 28	5 : 82
30	3 : 35	4 : 33	3 : 00	4 : 18	4 : 50	6 : 01

Total ozonide: Total ozonide precipitate obtained from CCl_4 solution by the addition of petroleum ether, yield 19.68 g.

F_A: Precipitate obtained by the addition of 15 c.c. petroleum ether to 50 c.c. benzene solution of the total ozonide precipitate, yield 11.22 g. (57%).

F_B: Precipitate obtained by the addition of 25 c.c. petroleum ether to the mother liquor of F_A, yield 7.12 g. (36%).

b) Ozonide prepared in Benzene

Time elapsed (hrs.)	Flow Time (min. : sec.)					
	Total ozonide		F_A (hexamer)		F_B (tetramer)	
	0.066 M	0.145 M	0.066 M	0.145 M	0.066 M	0.145 M
0	0 : 54	0 : 56	0 : 54	0 : 56	0 : 54	0 : 56
3	1 : 10	1 : 19	1 : 04	1 : 12	1 : 15	1 : 23
6	1 : 24	1 : 35	1 : 21	1 : 35	1 : 40	1 : 53
9	1 : 43	2 : 01	1 : 32	1 : 56	2 : 06	2 : 30
12	2 : 00	2 : 24	1 : 40	2 : 16	2 : 30	3 : 00
15	2 : 16	2 : 53	2 : 04	2 : 35	2 : 54	3 : 32
21	2 : 52	3 : 42	2 : 34	3 : 17	3 : 46	4 : 35
24	3 : 12	4 : 13	2 : 40	3 : 41	4 : 10	5 : 03
27	3 : 26	4 : 41	3 : 04	4 : 03	4 : 34	5 : 39
30	3 : 46	5 : 04	3 : 20	4 : 25	5 : 02	6 : 12

Total Ozonide: Total ozonide precipitate obtained from benzene solution by the addition of petroleum ether, yield 20.16 g.

F_A: Precipitate obtained by the addition of 15 c.c. petroleum ether to 50 c.c. benzene solution of the total ozonide precipitate, yield 12.43 g. (62%).

F_B: Precipitate obtained by the addition of 25 c.c. petroleum ether to the mother liquor of F_A, yield 5.05 g. (25%).

c) Ozonide prepared in Chloroform

Time elapsed (hrs.)	Flow Time (min. : sec.)					
	Total ozonide		F_A (tetramer)		F_B (dimer)	
	0.066 M	0.145 M	0.066 M	0.145 M	0.066 M	0.145 M
0	0 : 52	0 : 55	0 : 52	0 : 55	0 : 52	0 : 55
3	1 : 24	1 : 32	1 : 20	1 : 32	1 : 25	1 : 40
6	1 : 42	2 : 07	1 : 43	2 : 05	2 : 02	2 : 21
9	2 : 12	2 : 52	2 : 08	2 : 43	2 : 40	3 : 02
12	2 : 38	3 : 26	2 : 32	3 : 21	3 : 15	3 : 44
15	3 : 06	4 : 03	2 : 58	3 : 57	3 : 51	4 : 30
21	4 : 02	5 : 22	3 : 48	5 : 11	5 : 03	6 : 03
24	4 : 25	6 : 08	4 : 15	5 : 53	5 : 36	6 : 53
27	4 : 54	6 : 44	4 : 43	6 : 30	6 : 02	7 : 46
30	5 : 25	7 : 23	5 : 08	7 : 08	6 : 42	8 : 41

Total Ozonide: Total ozenide precipitate obtained from Chloroform solution by the addition of petroleum ether, yield 18.95 g.

F_A: Precipitate obtained by the addition of 30 c.c. petroleum ether to 50 c.c. benzene solution of the total ozonide yield 10.98 g. (58%).

F_B: Precipitate obtained by the addition of 40 c.c. petroleum ether to the mother liquor of F_A, yield 6.43 g. (34%).

d) Ozonide prepared in Ethyl Ether

Time elapsed (hrs.)	Flow Time (min. : sec.)					
	Total ozonide		F_A (dimer)		F_B (dimer)	
	0.066 M	0.145 M	0.066 M	0.145 M	0.066 M	0.145 M
0	0 : 52	0 : 55	0 : 52	0 : 55	0 : 52	0 : 55
3	1 : 32	1 : 50	1 : 30	1 : 45	1 : 32	1 : 50
6	2 : 15	2 : 40	2 : 13	2 : 33	2 : 21	2 : 45
9	3 : 00	3 : 34	2 : 56	3 : 28	3 : 03	3 : 51
12	3 : 38	4 : 24	3 : 36	4 : 18	3 : 37	4 : 42
15	4 : 21	5 : 21	4 : 14	5 : 10	4 : 32	5 : 38
21	5 : 46	7 : 20	5 : 36	7 : 02	6 : 00	7 : 45
24	6 : 32	8 : 23	6 : 12	8 : 03	6 : 47	8 : 53
27	7 : 17	9 : 32	6 : 57	9 : 05	7 : 31	10 : 05
30	8 : 00	10 : 43	7 : 40	10 : 08	9 : 16	11 : 35

Total Ozonide: Total ozonide precipitate obtained from ethyl ether solution by the addition of petroleum ether, yield 19.68 g.

F_A: Precipitate obtained by the addition of 80 c.c. petroleum ether to 50 c.c. benzene solution of the total ozonide, yield 8.31 g. (42%).

F_B: Precipitate obtained by the addition of 70 c.c. petroleum ether to the mother liquor of F_A, yield 7.90 g. (40%).

greatest extent that is approximately the same as the activity of the peroxide monomer. F_B of carbon tetrachloride and of benezene or F_A of chloroform which contain tetramer induce acceleration intermediate between hexamer and dimer. It may, therefore, be concluded that the activity decreases as the number of monomer polymerized increases.

b) *Reduction of Permanganate.* Fractions of the hexamer, tetramer and dimer used for the present experiment are the same as those employed in the previous one. Each fraction is added to 2×10^{-5} molar potassium permanganate in 1 N sulfuric acid so that the concentration of the polymers may be 6×10^{-4} molar when calculated as monomer. The time required for the just complete decolorization of the permanganate is determined, which can be taken as the measure of the reduction velocity.

Table 5. Time required for the Complete Reduction of Permanganate (room temperature)

Solvent	Dipole moment $\mu\times10^{18}$	Total Ozonide		F_A		F_B	
		n	Time of reduction (sec.)	n	Time of reduction (sec.)	n	Time of reduction (sec.)
CCl_4	0	6–4	105	6	135	4	64
C_6H_6	0	6–4	92	6	123	4	56
$CHCl_3$	0.95	4–2	26	4	25	2	10
$C_2H_5OC_2H_5$	1.10	2	1	2	4	2	2

It has been found by this experiment that the hexamer fractions require for the reduction 125–135 sec., the tetramer fractions 35–64 sec., and the dimer fractions 2–10 sec. This shows that the reducing activity decreases as the number of monomer polymerized increases, which is in accord with the results of the previous experiment.

Summary.

Styrene ozonide has been prepared by introducing purified ozonized air into styrene dissolved in carbon tetrachloride, in benzene, in chloroform, and in ethyl ether.

The ozonide thus prepared does not oxidise styrene but promotes its polymerization. The increase of the ozonide concentration in styrene shortens the activation period but not the polymerization period. Temperature effect upon this polymerization is also seen to be exerted only upon the activation stage. Among the decomposition products of styrene ozonide, benzaldehyde and polystyrene slightly accelerate the styrene polymerization but benzoic acid, formic acid and formaldehyde are inactive in this respect.

The ozonides prepared in the four different solvents have been examined for their molecular weight by the measurements of freezing point and of viscosity. It has been found that they are not the simple ozonide but its polymers; those prepared in carbon tetrachloride and in benzene consist of hexamer and tetramer, that prepared in chloroform tetramer and dimer, and that prepared in ethyl ether only dimer. Thus, the solvent of higher dipole moment gives the lower polymer.

Both chemical and physical properties of the ozonide differ according to the stage of polymerization, higher polymer is less active for styrene polymerization and for permanganate reduction, the lower the stage of polymerization its chemical activity is more closely related to peroxide monomer. Higher polymer has higher viscosity than the lower.

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