

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATALYSIS OF POLYMERIZATION BY OZONIDES

BY RAY C. HOUTZ AND HOMER ADKINS

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In view of the important part oxygen apparently plays in the drying of oils, and in the polymerization of various substances such as styrene and isoprene,¹ it seemed worth while to study the action of ozonides in accelerating polymerizations. In addition to the metal halides which are well known as polymerization catalysts, many apparently unrelated materials have been claimed to catalyze the polymerization of dienes, such for example, as alkaline earth alkyls,² glycerol, starch, urea,³ organic peroxides, acid anhydrides, metal oxides and per-salts,⁴ and the products obtained by ozonizing isoprene.⁵ Since the completion of the experimental work discussed in this paper, Conant and Tongberg⁶ have shown that a partially ozonized sample of isoprene polymerized more rapidly at ten to twelve thousand atmospheres' pressure than did unozonized isoprene.

The material used as a catalyst in this investigation was a mixture of the ozonides of two octylenes known as "diisobutylene."⁷ It was prepared by passing a mixture of 5% ozone and 95% oxygen into the hydrocarbon at 0–5° without a solvent. The reaction was considered complete when quantitative absorption of the ozone ceased, as shown by the effect of the issuing gas on starch-iodide paper. The product was a viscous, pale yellow oil, having on the average n_D^{25} 1.4425; d_{25}^{25} 0.9707. It was miscible with the common organic solvents and exploded if heated above 50–60°. Upon standing, it decomposed slowly with effervescence, losing its yellow color and explosiveness, decreasing markedly in viscosity, density, and refractive index, and increasing in acidity.

Since the formation of polymers results in an increase in the viscosity of a liquid or solution, viscosity measurements were made in order to compare the rates of polymerization.⁸ In general, the method consisted in sealing the samples in test-tubes from which the air had been displaced by a stream of nitrogen. The viscosity of each sample was measured at 25°

¹ Engler, *8th Int. Congr. Appl. Chem.*, 25, 661 (1912).

² Badische Anilin und Soda Fabrik, German Patent 255,786 (Jan. 27, 1912).

³ Farbenfabriken vom Friedr. Bayer & Co., German Patent 248,399 (March 24, 1911).

⁴ Chemische Fabrik Griesheim Elektron, German Patent 281,688 (April 2, 1914); Klätte and Rollet, U. S. Patent 1,241,738 (Oct. 2, 1918).

⁵ Badische Anilin und Soda Fabrik, British Patent 22,454 (Oct. 11, 1911); Holt and Steimmig, U. S. Patent 1,189,110 (June 27, 1916).

⁶ Conant and Tongberg, *THIS JOURNAL*, 52, 1659 (1930).

⁷ McCubbin and Adkins, *ibid.*, 52, 2547 (1930).

⁸ Cf. Stobbe and Posnjak, *Ann.*, 371, 259 (1909).

using an Ostwald viscometer. The tubes were allowed to stand for a time, then broken open and the viscosity redetermined. Each accepted flow-time was the average of four to six trials which checked within 0.1 or 0.2 seconds. Freshly made ozonide was always used in preparing the samples.

TABLE I
CATALYTIC POLYMERIZATION OF STYRENE AND INDENE, EFFECT OF SOLVENT AND TEMPERATURE

Catalyst concn., %	Solution	Temp., °C.	Reaction time	Viscosity Data		
				Flow time		% increase
				(On sealing)	(On opening)	
Styrene						
None	10% in toluene	100	6 Hrs.	106.6 (a)	106.9	0.3
None	10% in toluene	100	6 Hrs.	106.6 (a)	107.2	0.6
1	10% in toluene	100	6 Hrs.	108.1 (a)	140.1	29.6
1	10% in toluene	100	6 Hrs.	108.1 (a)	139.9	29.4
None	10% in toluene	100	10 Hrs.	106.3 (a)	118.4	11.5
None	10% in toluene	100	10 Hrs.	106.3 (a)	117.6	10.7
1	10% in toluene	100	10 Hrs.	107.7 (a)	150.7	40.0
1	10% in toluene	100	10 Hrs.	107.7 (a)	151.0	40.2
None	10% in toluene	Room	46 Days	43.6 (b)	43.5	-0.2
2	10% in toluene	Room	46 Days	44.5 (b)	47.6	7.0
None	5% in toluene	Room	6 Days	37.3 (c)	37.1	-0.5
None	5% in toluene	Room	6 Days	37.3 (c)	37.2	-0.3
1	5% in toluene	Room	6 Days	37.6 (c)	38.3	1.9
1	5% in toluene	Room	6 Days	37.6 (c)	38.4	2.2
Indene						
None	No solvent	100	22 Hrs.	111.2 (b)	115.3	3.7
None	No solvent	100	22 Hrs.	111.2 (b)	115.8	4.1
3	No solvent	100	22 Hrs.	114.6 (b)	183.9	60.5
3	No solvent	100	22 Hrs.	114.6 (b)	180.1	57.0
None	10% in toluene	100	22 Hrs.	112.1 (a)	112.5	0.4
None	10% in toluene	100	22 Hrs.	112.1 (a)	112.6	0.5
1	10% in toluene	100	22 Hrs.	113.7 (a)	115.6	1.7
1	10% in toluene	100	22 Hrs.	113.7 (a)	115.0	1.1

The flow time for water of viscometer (a) was 149.4 sec., for (b) 59.3 sec. and for (c) 50.6 sec.

Polymerization of Styrene.⁹—Preliminary experiments showed that a small concentration of the ozonide caused styrene to polymerize rapidly, the mixture becoming almost solid in the course of a week. A study was then made of the effect of catalyst concentration on the rate of polymerization. Solutions containing from 0 to 4% ozonide in styrene were placed in a thermostat at 25°. The rates of viscosity increase of styrene using various amounts of catalyst are shown in Fig. 1. The viscometer first used has a water-flow time of 59.3 seconds, but as the viscosities increased the flow times became too large to be convenient, so another having a much shorter flow time was employed. The flow times shown in Fig. 1 are all

⁹ Cf. Staudinger and Heuer, *Ber.*, 63, 222 (1930).

calculated to the first viscometer on the basis of the flow times of sulfuric acid through the two viscometers. The data in Fig. 1 show that increased concentration of ozonide up to 2% was very effective in increasing the rate of polymerization but that increasing the concentration of catalyst beyond this amount had little effect. The 0.5% curve seems to indicate that an induction period was necessary, since nearly two hundred hours elapsed before a rapid viscosity increase began. Stobbe and Posnjak⁸ found that styrene which had stood for fourteen days was polymerized more rapidly by heat and light than freshly distilled styrene. Probably styrene becomes activated toward polymerization upon standing.

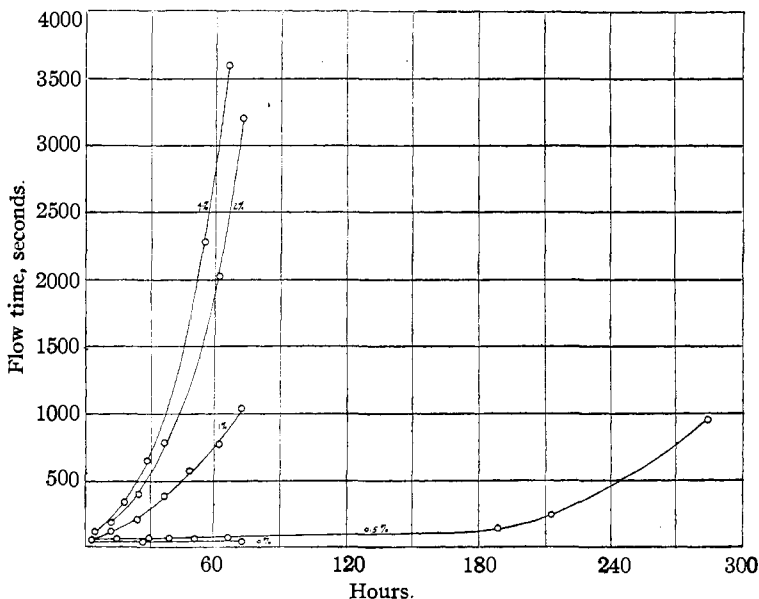


Fig. 1.—Relation of concentration of ozonide to rate of polymerization of styrene. The viscosities at 25° of four samples of styrene containing 0.5, 1, 2 and 4%, respectively, of diisobutylene ozonide are plotted against the time in hours elapsing after the addition of the latter to the styrene.

To determine whether the catalyst was active at elevated temperatures, tubes containing 0, 1 and 4% ozonide were sealed and placed in a steam jacket (nearly 100°) for thirty minutes. The contents of the tubes containing 1 and 4% ozonide had become almost solid. The styrene in the tubes containing no ozonide had thickened considerably, but less than those into which the catalyst had been introduced. The polymerization of styrene was also studied in toluene solution, at both room temperature and 100°. An abstract of the data is given in Table I. The changes in viscosity show that the catalyst was active toward styrene in toluene solution, at both temperatures.

Polymerization of 2,3-Dimethylbutadiene-1,3.—Solutions containing from 0 to 4% ozonide in freshly distilled dimethylbutadiene were made and left in sealed tubes at room temperatures for forty-four days. The viscosity increases noted were as follows: for 0% ozonide, 63.5, 67.5%; 0.125% ozonide, 83.0, 81.0%; 0.25% ozonide, 93.5, 90.5%; 0.5% ozonide, 100, 99%; 1.0% ozonide, 118, 114%; 2.0% ozonide, 114, 111%; 4.0% ozonide, 117, 122%. It is apparent that the catalytic power of the ozonide toward the diene increased with increasing concentration, but that increments became decreasingly effective, just as was found in the case of styrene.

Polymerization of "Methylpentadiene."—Tubes were sealed containing 0.0 and 3.0% of ozonide in methylpentadiene, and allowed to stand for ninety days at room temperature. The increases in viscosity were as follows: 0% catalyst, 1.2% increase; 3% catalyst, 10.4% increase. This result was confirmed by the fact that there was much more of the sticky, rubber-like polymer left on evaporation of the sample containing 3% ozonide than there was from the sample containing no ozonide.

Polymerization of Indene.—Samples were sealed and allowed to stand for thirty days. After measuring viscosity they were resealed and left for one hundred and twenty days longer. The percentage increases in viscosity during thirty days were as follows: 0% ozonide, 0.3, 0.7%; 2% ozonide, 12.9, 14.0%; at the end of one hundred and fifty days, 0% ozonide, 3.0, 2.7%; 2% ozonide, 50.5, 56%. The data in Table I show that the ozonide is catalytically active toward indene at 100° as well as at room temperature, and also in toluene solution.

Polymerization of Furfuryl Alcohol.—Since furfuryl alcohol turns dark with the formation of resinous products on contact with air, the effect of the ozonide on this substance was studied both in air and in nitrogen. Tubes were sealed and allowed to stand at room temperature for forty days. In the tubes containing nitrogen, the viscosity increases were as follows: 0% catalyst, 1.0, 2.1%; 2% catalyst, 45.6, 47.2%. In the tubes containing air: 0% catalyst, 21.6%; 2% catalyst, 62.4, 66.4%. The percentage of increase in the tubes containing both catalyst and air is approximately the sum of the separate effects of catalyst and air. Since the ozonide liberates some oxygen as it decomposes on standing, the polymerizing effect may be due merely to the presence of the liberated molecular oxygen.

Attempted Polymerization of Other Compounds.—Solutions containing 2% ozonide in trimethylethylene and diisobutylene were sealed and allowed to stand for three to four months. No significant viscosity change had occurred during that time. Stilbene and saligenin were studied similarly in solution using dibutyl ether, dioxane, and toluene as solvents. When no significant viscosity change occurred in three months at ordinary temperatures, higher temperatures were employed (60 and 100°). Viscosity changes in all cases were too small to be significant.

Deterioration of Catalyst.—A sample of ozonide which had stood for several months was found to be active toward styrene. If the ozonide itself is concerned with the catalytic effect, fresh samples should be more active than old ones. If, on the contrary, decomposition products are more active, the catalytic power should increase somewhat on standing. To test this point, the catalytic power of the ozonide was measured on five successive days and again after an interval of twelve days, by noting the viscosity increase produced in freshly distilled styrene samples in twenty-four hours. Each day a fresh solution of the ozonide in styrene was made, and the viscosity increase produced in twenty-four hours noted. Both ozonide and solutions were kept in a thermostat at 25°. The results are plotted in Fig. 2. The decrease in viscosity of the ozonide was very rapid for about three days and during this time the catalytic power decreased rapidly. If decrease in viscosity may be taken as a measure of the decomposition of the ozonide, the latter parallels the decrease in catalytic power, indicating that the ozonide itself,

rather than decomposition products, is concerned with the catalysis of polymerization. If ozonization of diisobutylene is stopped just at the point at which quantitative absorption ceases, the ozone has a very high viscosity. If stopped before this point is reached, the product is much less viscous, due, no doubt, to the presence of diisobutylene. If ozonization is carried beyond this point, the product is also less viscous. This may be due to the formation of perozonides and oxidation products, as indicated by the work of Brus and Peyresblancques.¹⁰

Preparation of Reagents.—Diisobutylene was prepared as by Edgar.¹¹ Styrene was prepared as by Abbot and Johnson.¹² 2,3-Dimethylbutadiene-1,3 was prepared from pinacol in 60% yield.¹³ Stilbene was prepared essentially according to the method

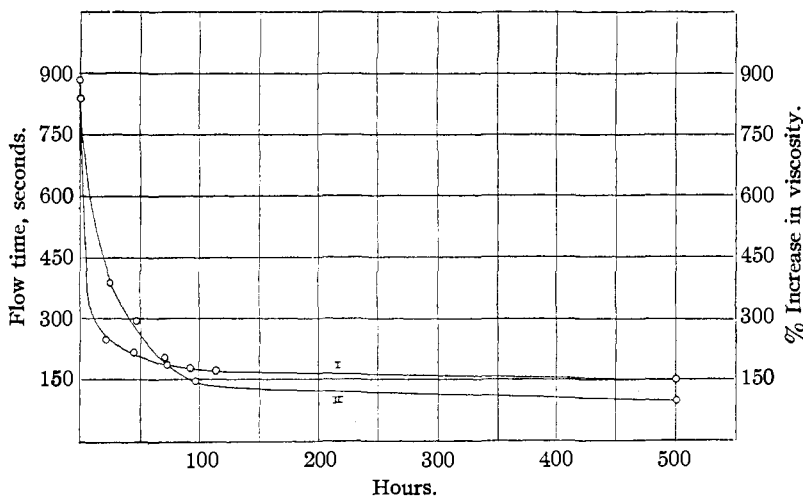


Fig. 2.—Relation of age to catalytic activity of ozonide. In curve I the viscosity of diisobutylene ozonide (expressed in flow time in seconds) is plotted against the time in hours that had elapsed after its preparation. In curve II there is plotted the percentage increase in the viscosity after twenty-four hours at 25° of a sample of styrene containing 2% of ozonide, against the hours that had elapsed between the preparation of the ozonide and its addition to the sample of styrene.

of Hell.¹⁴ Saligenin (*o*-hydroxybenzyl alcohol, m. p. 84°) was obtained by hydrogenation of salicylaldehyde over nickel.¹⁵ The aldehyde (56 g.) was prepared from 250 g. of phenol by the method of Reimer and Tieman.¹⁶ Trimethylethylene (34–38°) was obtained from tertiary amyl alcohol.¹⁷ Methylpentadiene was prepared by the dehydration of 2-methylpentadiol-2,4. The latter was obtained by the reduction of diacetone alcohol. Eighty-three grams of the diol were dehydrated using 1.4 g. of aniline

¹⁰ Brus and Peyresblancques, *Compt. rend.*, **190**, 685 (1930).

¹¹ Edgar, *Ind. Eng. Chem.*, **19**, 145 (1927).

¹² Abbot and Johnson, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII. p. 84.

¹³ Kyriakides, *THIS JOURNAL*, **36**, 992 (1914).

¹⁴ Hell, *Ber.*, **37**, 453 (1904).

¹⁵ Adkins and Cramer, *THIS JOURNAL*, **52**, 4354 (1930).

¹⁶ Reimer and Tieman, *Ber.*, **9**, 824 (1876).

¹⁷ Earl, *J. Proc. Roy. Soc. N. S. Wales*, **61**, 68 (1927).

hydrobromide as a catalyst as in the preparation of 2,3-dimethylbutadiene-1,3. The oil layer was found to boil at 72-128°. The formation of some of a methylpentenol was indicated by the fact that the weight of the water layer was low as well as by the boiling range of the product. An attempt to complete the dehydration with oxalic acid resulted in the formation of dark, high-boiling products. About 15 g. of olefin boiling at 74-76° was collected as a mixture of two possible methylpentadienes.

Summary

A mixture of the ozonides of two octylenes has been found to catalyze the polymerization of styrene, indene, 2,3-dimethylbutadiene-1,3, a methylpentadiene, and furfuryl alcohol. It has been found to be inactive as a polymerization catalyst toward stilbene, *o*-hydroxybenzyl alcohol, trimethylethylene, and the mixture of octylenes from which it is made. The catalyst was active at room temperature and 100° and in a solution in toluene. The ozonide underwent a change on standing especially during the first two days after its preparation and lost a large part of its catalytic power.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

CHARACTERIZATION OF ALKYL HALIDES AND ORGANOMAGNESIUM HALIDES¹

BY A. M. SCHWARTZ AND JOHN R. JOHNSON

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Since organomagnesium halides react smoothly with aryl isocyanates to produce substituted amides that are usually crystalline solids, this reaction is suitable for the identification of organomagnesium halides and of halides that can be converted into these. Gilman and his collaborators² have used phenyl and α -naphthyl isocyanates for this purpose and have pointed out that α -naphthyl isocyanate enjoys some advantages over phenyl isocyanate. The most important of these appears to be the fact that the resulting α -naphthyl amides can be purified more readily than the anilides. This disadvantage attending the use of phenyl isocyanate can be minimized by avoiding an excess of the isocyanate and is more than counterbalanced, in our experience, by the fact that only a small number of the α -naphthyl amides are described in the literature. Of the ten α -naphthyl amides prepared by Gilman and Furry, five had not previously been reported. On the other hand, the anilides of all of these

¹ A paper presented at the St. Louis Meeting of the American Chemical Society, April 18, 1928. The present report contains additional data not included in the preliminary paper.

² Gilman and Furry, *THIS JOURNAL*, 50, 1214 (1928). This article gives an excellent review of previous work dealing with the action of aryl isocyanates on organometallic halides.