[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKLYN COLLEGE]

STUDIES ON THE DIMERIZATION OF STYRENE IN AQUEOUS SULFURIC ACID

MILTON J. ROSEN

Received June 11, 1953

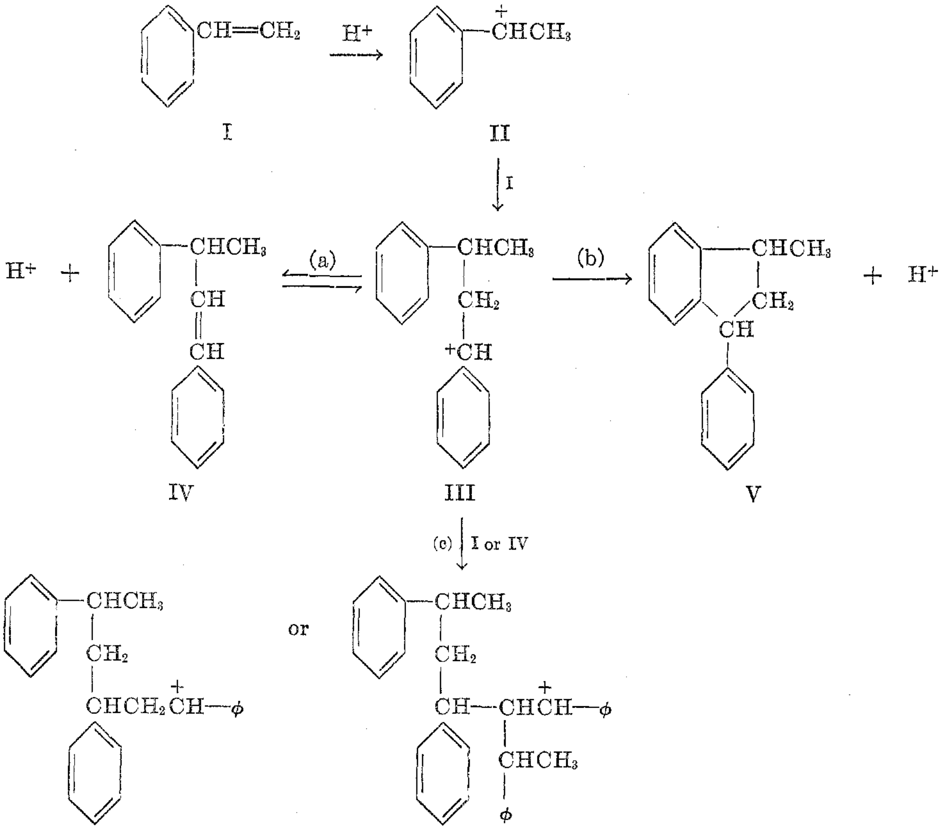
In a continuation of our investigation into the properties of styrene dimers, it was decided to study the reaction by means of which the dimers were prepared. We had confirmed (1) the observations of Risi and Gauvin (2) that treatment of monomeric styrene with ten volumes of 5:4 (wt.) sulfuric acid solution (= 53% H_2SO_4) at reflux temperature yielded a mixture of dimers [containing predominantly the unsaturated dimer, 1,3-diphenylbutene-1 (IV), along with the cyclic dimer, 1-methyl-3-phenylindane (V)], and the observation of Stoermer and Kootz (3) that ten volumes of a 1:1 (vol.) sulfuric acid solution (= 62% H_2SO_4) converted this mixture of dimers to a product containing only the cyclic dimer. It seemed to us that it might be possible to prepare the cyclic dimer directly from monomeric styrene, rather than through the intermediate formation of the mixture of dimers, by refluxing monomeric styrene with 62% H_2SO_4. This proved to be the case (Table I, Run 1). It appeared then that heating styrene with 53% H_2SO_4 at reflux temperature yielded a mixture of dimers, whereas similar treatment with 62% H_2SO_4 yielded only the cyclic dimer. In an attempt to find an explanation for this phenomenon, it was decided to investigate the factors which contribute to the formation of the unsaturated dimer, the cyclic dimer, and the various amounts of higher polymers (mainly trimers) which always accompany the dimers, in aqueous solutions of sulfuric acid. A series of reactions were run in which reaction time and temperature, and volume and concentration of the sulfuric acid solution, were all varied (Table I). Since this is a heterogeneous reaction, and the refractive indices of the products of the reaction are additive, the course of the reaction was followed by measuring the change in refractive index (n_D^{20}) of the oil phase. A number of typical runs are shown in Figure 1.

These data indicate that the formation of the three main products of the reaction—unsaturated dimer, cyclic dimer, and higher polymeric material—may be described as follows:

1. The monomer (I) dissolves in the aqueous sulfuric acid solution to form the corresponding carbonium ion (II), which reacts rapidly with additional dissolved monomer to yield the carbonium ion of the dimer (III). This reaction is independent of the concentration of unreacted monomer in the oil phase, since the change in refractive index of the oil phase with time is constant during this initial period (Figure 1), indicating a zero-order reaction probably dependent solely on the extent to which the monomer can dissolve in the aqueous phase. A state of saturation probably exists in the latter and new monomer dissolves only as monomer already in solution reacts and is removed as dimer or higher polymer.

2. The carbonium ion of the dimer immediately reacts by a number of routes:

(a) reversible loss of a proton to form the unsaturated dimer (IV), (b) irreversible cyclization and loss of a proton to form the isomeric cyclic dimer (V), and (c) formation of high polymers by reaction with additional unchanged monomer or unsaturated dimer.



Reaction (a) is fast under these conditions, as is evidenced by the immediate, rapid increase in the refractive index of the oil phase (Figure 1). That this increase is due mainly to the presence of unsaturated dimer was shown by runs which were stopped after a short reaction period (Runs 7 and 12). Since this reaction is rapid, it is to be expected that the over-all yield of unsaturated dimer will be favored by conditions which decrease the rates of the competitive reactions (b) and (c), such as lower reaction temperature (Runs 5 and 6), and sulfuric acid solutions of lower concentration (Runs 6 and 11).

Reaction (c) is also rapid under these conditions, as is evidenced by the large amount of polymeric material which may be obtained in a relatively short time (Run 7) and its indifference to temperature change in the range studied (Runs 5, 6, and 7). Moreover, since our data show very little or no increase in higher polymeric material with increase in reaction time (Runs 11 and 12; 5, 6, 7), this reaction is apparently confined mainly to the early stages of the over-all reaction. This would indicate that under these conditions reaction (c) involves a reaction of the dimer carbonium ion mainly with the monomer—which would be available only during the early stages of the over-all reaction—rather than with the unsaturated dimer. In spite of its indifference to temperature change, the rate of this reaction is markedly increased by an increase in the acidity of the aqueous phase (Runs 6 and 11) and a diminution of its volume (Runs 2, 3, 4, and 5). The former effect may be due to the increased solubilities of the unsaturated dimer and the monomer in sulfuric acid solutions of higher concentration. The latter effect is still unexplained, but may possibly be due to solubilization of the sulfuric acid under these conditions by the oil phase, with the consequence that reaction would then occur in the oil phase, where the opportunity for higher polymer formation is far greater.

TABLE I

DIMERIZATION OF STYRENE IN AQUEOUS SULFURIC ACID

RUN NO.	CONDITIONS		TEMP., (°C.)	TIME (hr.)	PRODUCTS[a]		
	% H_2SO_4 (wt.) in aqueous phase	$\frac{\text{Vol. aqueous phase}}{\text{Vol. oil phase}}$			SATURATED DIMER, %	UN-SATURATED DIMER, %	HIGHER POLYMERS, %
1	62	10	144–147	48	53 (?)	0	not determined
2	62	10	144–146	15⅔	74	0	26
3	62	1	143–147	10	49	5	46
4	62	3	143–147	13	56	1	43
5	62	5	143–146	14	71	0	29
6	62	5	126–127	10½	47½	22½	30
7	62	5	106–107	3	18	51	31
11	53	5	116–127	10½	15½	70	14½
12	53	5	116–127	4	7	80	13
15	53	5	116–127	4	81	0	19
	62	5	145–147	12			
16	46	5	107	4½	78	0	22
	62	5	145–147	6½			

[a] Percentages of the dimers are based on the refractive indices of the dimer fraction of the distilled reaction mixture. Synthetic mixtures of the pure unsaturated dimer and the pure cyclic dimer proved that the mixed refractive indices are additive. Percentages of higher polymers are based on weights of residues left in the distillation flask after removal of the dimer fraction.

Reaction (b), as compared to (a) and (c), is rather slow. Those runs which were stopped after a few hours (Run 7 and 12) showed minor yields of cyclic dimer. However, since reaction (a) is easily reversible, involving only solubilization of the unsaturated dimer in the aqueous acid and addition of a proton, and reaction (b) is difficultly, if at all reversible, an increase in reaction time always shows an increase in yield of cyclic dimer at the expense of the unsaturated, even under conditions favoring formation of the latter (Runs 11 and 12). It is this conversion of unsaturated to cyclic dimer which was observed by Stoermer and Kootz (3). Since conditions which promote solubility of the unsaturated dimer in the aqueous phase will increase the rate of its conversion to the cyclic dimer, it is to be expected that an increase in the sulfuric acid concentration of the aqueous phase will result in an increased yield of the latter (Runs 6 and 11). An increase in reaction temperature also results in an increased yield of cyclic dimer (Runs 5 and 6), probably because the general increase in reaction rates which it produces increases the rate of reversal of reaction (a) and the rate of irreversible (b).

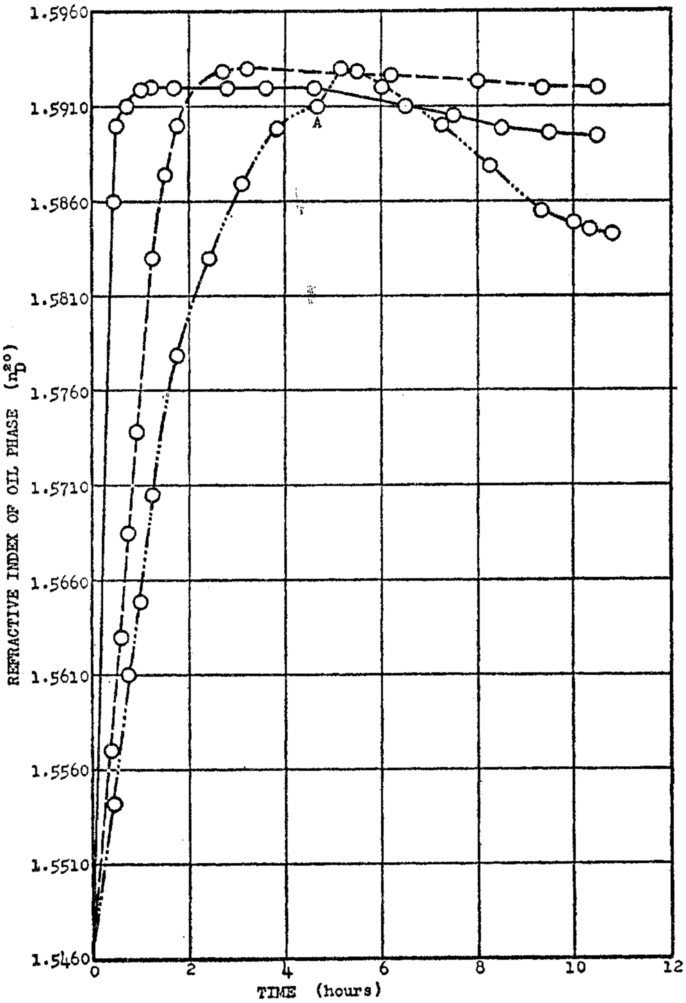


FIG. 1. CHANGE IN REFRACTIVE INDEX OF THE OIL PHASE DURING DIMERIZATION OF STYRENE IN AQUEOUS SULFURIC ACID. ——— Run 6, Table I; - - - Run 11; -···Run 16. Additional conc'd sulfuric acid was added at point A, Run 16.

Our interpretation of the over-all reaction was tested by two runs in which we attempted to obtain a maximum yield of cyclic dimer. The problem here was that one of the conditions which favored formation of the cyclic dimer (sulfuric acid solutions of high concentration) also favored the formation of higher polymers. However, since our data indicated that the major amount of high polymers was formed by reaction of the carbonium ion of the dimer with monomer during the early stages of the reaction, we attempted to achieve our purpose by using sulfuric acid solutions of relatively low concentration during the early stages of the reaction in order to minimize formation of the higher polymers, and solutions of higher concentration during the later phases, in order to effect conversion of unsaturated dimer to cyclic. As high a temperature as convenient (reflux temperature) was used in all stages of the reaction, since we had found that increased temperature, while favoring formation of saturated dimer, did not affect the yield of high polymer. The results obtained under these conditions (Runs 15 and 16, Table I) indicate that although high polymer formation cannot be eliminated, it can be minimized by this procedure.

EXPERIMENTAL

General procedure for the dimerization reaction. The freshly-distilled monomeric styrene (50 g. was usually used) was added to the sulfuric acid solution in a 3-necked flask equipped with a sealed stirrer, a reflux condenser, and a thermometer dipping into the reaction mixture. The flask and contents were stirred vigorously and maintained at the appropriate temperature with an electrically-heated oil-bath. Samples of the reaction mixture were withdrawn with a bulb pipette at appropriate intervals, the oil layer of the sample was allowed to separate, and its refractive index was measured. The refractive index of the oil as determined in this manner was not significantly different from that obtained after washing the oil with sodium bicarbonate solution and water.

After the reaction had been stopped, the reaction mixture was diluted with an equal volume of water, and the oil layer was allowed to separate. The aqueous acid layer was extracted three times with ether, the ether extracts were combined with the oil layer, and the whole was washed successively with a saturated solution of sodium bicarbonate, water, and a saturated calcium chloride solution, and dried over calcium chloride. After removal of the ether, the residual material was distilled through a 12″ Vigreaux column. In no case was any fore-run of monomeric styrene obtained. The fraction boiling in the range of 154–167° (8 mm.) was considered dimer. [The pure cyclic dimer boils at 155° (8 mm.); the pure unsaturated dimer, 166° (8 mm.).] In the cases in which the cyclic was the only dimer present, the product had a boiling range of $<2°$. Material remaining in the flask after removal of the dimer was considered "high polymeric material".

In Runs 15 and 16 (Table I), the reaction was started using the lower concentration of sulfuric acid and after 4–4½ hours, concentrated sulfuric acid was added below the surface of the well-stirred reaction mixture in order to bring the acid in the aqueous phase to the desired concentration.

SUMMARY

A study has been made of the effect of time, temperature, and acidity upon the reaction of monomeric styrene with aqueous sulfuric acid.

An attempt has been made to explain the formation of the products obtained by varying these conditions.

BROOKLYN 10, NEW YORK

REFERENCES

(1) SPOERRI AND ROSEN, *J. Am. Chem. Soc.*, **72**, 4918 (1950).
(2) RISI AND GAUVIN, *Can. J. Research*, **B14**, 255 (1936).
(3) STOERMER AND KOOTZ, *Ber.*, **61**, 2330 (1928).