Table X. Activation Entropies (in eu)

Compound	Geometry of activated complex	$\Delta S^{\ddagger}$ at 273°K	$\Delta S^{\ddagger}$ at 423°K	$\Delta S^{\ddagger}$ at 573°K
Hexa-1,5-diene	Chair-like	−12.50	−16.58	−16.99
Hexa-1,5-diene	Boat-like	−12.65	−16.71	−17.13
cis-1,2-Divinylcyclo-propane	Boat-like	−5.50	−8.46	−8.60
cis-1,2-Divinylcyclo-butane	Boat-like	−6.60	−10.00	−10.34

certain ranges of values of ω_{Ca} two or more hydrogen atoms come so close that their interaction causes a tremendous increase of E_{nb}. The two curves correspond to the two pairs of values of $\omega_{aa'}$ and $\omega_{a'C'}$ corresponding to each value of ω_{Ca}. The energy of the chair is also shown in Figure 12, for comparison. The reaction enthalpy at 0°K turns out to be $\Delta H_0° = -18.7$ or -23.4 kcal/mol. Calorimetric work is in progress[37] to obtain an experimental result for comparison.

Since our method allows the determination of the geometry and bond orders in the activated complex for these reactions, taking advantage of the fact that only integer or half-integer bond numbers occur, for which the relevant data are available, we calculated the activation entropies for the reactions I–III (Figure 2) according to the standard statistical mechanics

(37) M. Simonetta, V. Rosnati, and V. Ragaini, work in progress.

method.[38] The results are collected in Table X. The only available experimental result for the reaction of divinylcyclobutane, calculated from published data,[36] is $\Delta S^{\ddagger} = -11.7$ eu at 373°K.

From the general outcome of our results it can be said that satisfactory agreement with experimental data obtains. These calculations support the previously proposed mechanism for the Cope rearrangement and allow a quantitative determination of the geometry of the activated complex with the presumed general shape. In particular, it is good that activation energy for the cyclobutane and cyclopropane derivatives are comparable and both are lower than the values for hexa-1,5-diene. Besides the two values for hexa-1,5-diene chair- and boat-like activated complex are in the right order and with the expected difference. Of course these results are far from being definitive owing to the many approximations included and the use of many physical constants. Further investigation should be carried out to find more rigorous and detailed ways of calculation. Nevertheless they seem to point an effective way to attack the problem of quantitative prediction of chemical reactivity.

(38) (a) A. Wasserman, *J. Chem. Soc.*, 612 (1942); (b) K. E. Lewis and H. Steiner, *ibid.*, 3080 (1964).

The Dimerization of Styrene[1]

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Abstract: The thermal polymerization of styrene at 150° gives both higher polymers and a mixture of dimers in largely independent reactions. Eleven C_{16} hydrocarbons have been identified in the dimer fraction. The proportions of these "dimers," the ratio of "dimer" to higher polymer, and the over-all rate of reaction depend on the promoter or inhibitor employed; iodine, sulfur, 2,4,6-trinitrobenzene, picric acid, and ultraviolet light have been tested. The uncomplicated dimerization is mostly a nonchain reaction, giving first 1,2-diphenylcyclobutane and 1-phenyltetralin. Several 1,3-diphenylbutenes arise from acid (or high iodine) catalysis or from free-radical chain reactions. Some of these butenes are hydrogenated to 1,3-diphenylbutane by 1-phenyltetralin, which is thus dehydrogenated to 1-phenyl-1,2-dihydronaphthalene and 1-phenylnaphthalene. Iodine catalyzes the formation of 1-phenyltetralin and sulfur promotes formation of 2,4-diphenyl-1-butene. The latter is also the lowest oligomer resulting from chain transfer of styrene with bromobenzene solvent (with little incorporation of solvent). From these results, new mechanisms for thermal initiation of polymerization and for chain transfer with aromatic solvents are proposed.

Previous work[2] on the thermal polymerization of styrene in refluxing bromobenzene has indicated the presence of two independent reactions. One is the well-known polymerization by a free-radical chain mechanism, with an apparent order near 2.5. The low polymer formed by this mechanism averages nearly one double bond per molecule. The other reaction is bi-

(1) Earlier and shorter versions of this paper were presented: *Intern. Symp. Macromol. Chem. Moscow, 1960*, II, 11 (1961); *Amer. Chem. Soc., Polymer Preprints*, 2 (2), 55 (1961).

molecular and nonchain. It leads to a dimer fraction that is more than 90% saturated and therefore cyclic. The earlier work[2] also showed that more dimer could be obtained by using an inhibitor (picric acid) than a diluent to retard the chain reaction. The primary object of the present work was to identify the dimer. However, the infrared absorption of the dimer fraction changed as the inhibitor was changed. This paper shows how the dimer fractions were resolved into several isomeric

dimers and some of their oxidation and reduction products. The results contribute to our understanding of the mechanisms of thermal initiation in the polymerization of styrene and of chain transfer of styrene with aromatic solvents.

Experimental Section

Procedure. In most experiments, 50–1000 g of styrene (less in 46, 47, and 50) containing inhibitor or catalyst was refluxed in an atmosphere of nitrogen. As the reflux temperature (initially 143°) rose during reaction, heat input was restricted so that the liquid temperature averaged within 2° of 150°. In some experiments, 14.2% by weight solutions of styrene in bromobenzene were refluxed at 144–157°. The dimer fractions (bp 100–140° (1 mm)) were usually separated from monomer and higher polymer by distillation at reduced pressure. Distillation of some trimer was necessary to remove nearly all the dimer from the higher polymer. When the proportion of dimer in the whole product was low, separation by distillation was difficult or incomplete. In such cases, after removal of most of the unreacted styrene, the polymer was precipitated three times from benzene by methanol. The liquors were then concentrated and the dimer was separated by distillation. The dimer distillates were analyzed by gas–liquid partition chromatography (glpc) on a 5 ft × 0.25 in. column with 20% of DC710 fluid on 60–80 mesh Chromosorb P at 215° with a helium flow rate of about 100 cc/min. Chromatography was repeated to isolate enough of each product for infrared examination. Some retention times are listed in Figure 1.

Identification of Products. The several products with which we are concerned are given identifying numbers in Figure 1. They were best distinguished by their infrared absorptions at 9–15 μ, shown there. Distinctive absorptions in other regions are also indicated. Differences in C–H bond absorptions at 3.2–3.5 μ may also be very useful, but we did not start collecting this information soon enough to utilize it. 2,4-Diphenylthiophene (14) had a much longer retention time than the dimers listed in Figure 1 and no trimers were ever eluted from the column. Separations of 2 and 13 and of 4 and 5 by glpc were incomplete, and glpc data are not available for some products. Distinctions or semiquantitative estimates were then made by infrared spectroscopy. The major difficulty in infrared analyses was the absence of strong and unique absorption bands for compounds 3, 6, and 7. (The 6.77-μ band, between the 6.68- and 6.86-μ bands for 5, was strong, sharp, and unique.) A representative procedure compared the absorbance of a distinctive (perhaps weak) band for one compound in a mixture with the absorbance in the pure compound, assuming that the uniformly strong 6.68- and 6.86-μ bands measured the total concentration of dimers.

Only partial separation of dimers could be effected by vacuum distillation on a Nester and Faust spinning-band column. Thus, a mixture of dimers from expt 25, 28, 36, 38 (like 39), and 39 (Table I) distilled between 113° (0.64 mm) and 126° (0.55 mm). All distillate fractions were mixtures, but the indicated order of increasing boiling points was compounds 7, 6, 9, and 10 (the same as for retention times in glpc).

The absorption curve for 1,3-diphenylbutane (8) agrees satisfactorily with the published curve.[3]

1-Phenyltetralin (6) was isolated in good yields from expt 21 and 24 (which employed 1 kg of styrene) by crystallization from petroleum ether (bp 30–60°) and recrystallization from absolute alcohol. The best fraction melted at 21–25°. It had the theoretical analysis (92.1% C, 7.78% H), gave 65% yield of benzoylbenzoic acid (by mixture melting point and neutral equivalent) on oxidation with CrO_3 in acetic acid at 50°, and was dehydrogenated to 1-phenylnaphthalene (10) in 80% yield by heating with sulfur (see below). The 1-phenylnaphthalene thus prepared melted at 19° but, in comparison with a purchased sample, melted higher and had less infrared absorption.

1,3-Diphenyl-1-butene (1) and the 1-methyl-3-phenylindans (5, cis and trans isomers not resolved) were prepared by the sulfuric acid catalyzed dimerization of styrene[4] (expt 37, A1) for use as standards.

The presence of 1,2-diphenylcyclobutane (7) in a styrene dimer fraction (made with 0.2% iodine as retarder) has been established by its oxidation to 1,2-dibenzoylethane.[5] We have since obtained 0.098 g of dibenzoylethane by a similar oxidation of 1.04 g of dimer fraction 36. Product 7 was also isolated by preparative gas chromatography and had the theoretical carbon and hydrogen analysis. This product has also been prepared by Levina, et al.,[6] from 3,6-diphenyl-1,4,5,6-tetrahydropyridazine, by Dodson and Zielske[7] by hydrogenation of 1,2-diphenylcyclobutene, and by Brown and Markezich[8] by sensitized dimerizations of styrene and by other methods described herein. The infrared absorption of 7 in Figure 1 corresponds to the *trans* isomer.[7,8]

The dimer fraction of expt 34 (with 1 mol % sulfur) was investigated carefully by Parkhurst, Rodin, and Silverstein.[9] From it they isolated and identified compounds 2, 3, 4, and 13. We did not ordinarily see or recognize *cis*-1,3-diphenyl-1-butene (2) in our work. Standinger and Steinhofer[10] obtained substantial yields of compounds 4, 11, and 13 by cracking polystyrene at 300°.

The structure of 1-phenyl-1,2-dihydronaphthalene (9) is based on its carbon and hydrogen analysis (intermediate between that of 6 and 10), its infrared absorption, the presence of products 6 and 10, and assignment of the 1,2-hydrogen atoms by Brown and Markezich.[8]

Products 4, 11, and 12 were made by polymerization of styrene in very dilute solution in bromobenzene (expt B14). The structure of 11[10] is inferred from comparison of its infrared absorption with that of product 4, a major constituent of the dimer fraction in the same run.

Dehydrogenations with sulfur were carried out by heating dimers to 250–270° until evolution of H_2S gas ceased (constant weight). In general, the open-chain dimers or their mixtures gave fair to good yields of crystallizable 2,4-diphenylthiophene (14), but cyclized dimers did not (6 gave 10; see above). A cut of the "trimer" fraction of expt 34, bp 148–54° (0.05 mm), gave 62% of 14 by such a procedure.

Heating styrene with sulfur at 230° is known[11] to give mostly 2,4-diphenylthiophene (14), a little 2,5-diphenylthiophene (15), and some ethylbenzene. We made 14 for a standard by heating 2.08 g of dimer 49 (mostly 8) with 1.29 g of sulfur for 2 hr at 230–260°; 0.54 g of crude crystals was obtained, mp 116–117°, after recrystallization from ethanol (lit.[11] mp 119–120°). 2,5-Diphenylthiophene (15) crystallized unexpectedly from one of the distillates of expt 42. It contained 81.2% C, 5.3% H, and 13.5% S by difference and melted at 148–149° (lit.[11] mp 152°).

By-Products. Oxygen-containing by-products formed in dimerizations with trinitrobenzene (TNB) and picric acid (PA) were removed before the analyses in Table I were made. Thus, in expt 36 the dimer fraction contained some new infrared absorption bands. On chromatography of 4.58 g of dimer fraction through 75 g of silica gel, elution with 150 ml of cyclohexane and then with cyclohexane + benzene gave 3.68 g of two very similar fractions having the total composition indicated in Table I. Elution with benzene then gave smaller quantities of unknown and colored compounds which could include (by infrared absorption) 4-phenyltetralone. Expt 39 used 340 g of styrene and 6.80 g of picric acid. Bronze crystals separated gradually during reaction; 5.6 g was separated by decantation and washed with petroleum ether. When similar material from expt 25 was recrystallized from nitrobenzene, it charred without melting at 250° and analyzed for 64.8% C, 4.02% H, 9.82% N, and (by difference) 21.36% O. This analysis corresponds to $C_{22}H_{16.3}N_{2.86}O_{5.43}$ (structure unknown, $2C_5H_8$ + $C_6H_3N_3O_6 - H_2O = C_{22}H_{17}N_3O_6$). On chromatography of 6.76 g of yellow dimer fraction from 39, 5.65 g of colorless dimer (Table I) was eluted with cyclohexane.

Polymerizations in Very Dilute Solution in Bromobenzene. This section describes two different kinds of experiments from further work on chain transfer in bromobenzene,[2] to be reported more fully elsewhere. In expts B1–B5, 26 g of styrene was refluxed in 6860

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(3) American Petroleum Institute Research Project 44, National Bureau of Standards, Washington, D. C., Serial No. 2151, 1959.

(4) P. E. Spoerri and M. J. Rosen, *J. Amer. Chem. Soc.*, 72, 4918 (1950); B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kutz, and H. I. Thayer, *J. Org. Chem.*, 19, 17 (1954).

(5) I. S. Bengelsdorf, *ibid.*, 25, 1468 (1960).

(6) R. Ya. Levina, Yu. S. Shabarov, M. G. Kuz'min, N. I. Vasil'ev, and E. G. Treshchova, *Dokl. Akad. Nauk SSSR*, 121, 303 (1958); *Chem. Abstr.*, 53, 1355 (1959).

(7) R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, 32, 28 (1967).

(8) W. G. Brown and R. L. Markezich, Abstracts of Papers, 153rd National Meeting of American Chemical Society, Miami Beach, Fla., April 1967, O-139, and private communications.

(9) R. M. Parkhurst, J. O. Rodin, and R. M. Silverstein, *J. Org. Chem.*, 28, 120 (1963).

(10) H. Standinger and A. Steinhofer, *Ann. Chem.*, 517, 35 (1935).

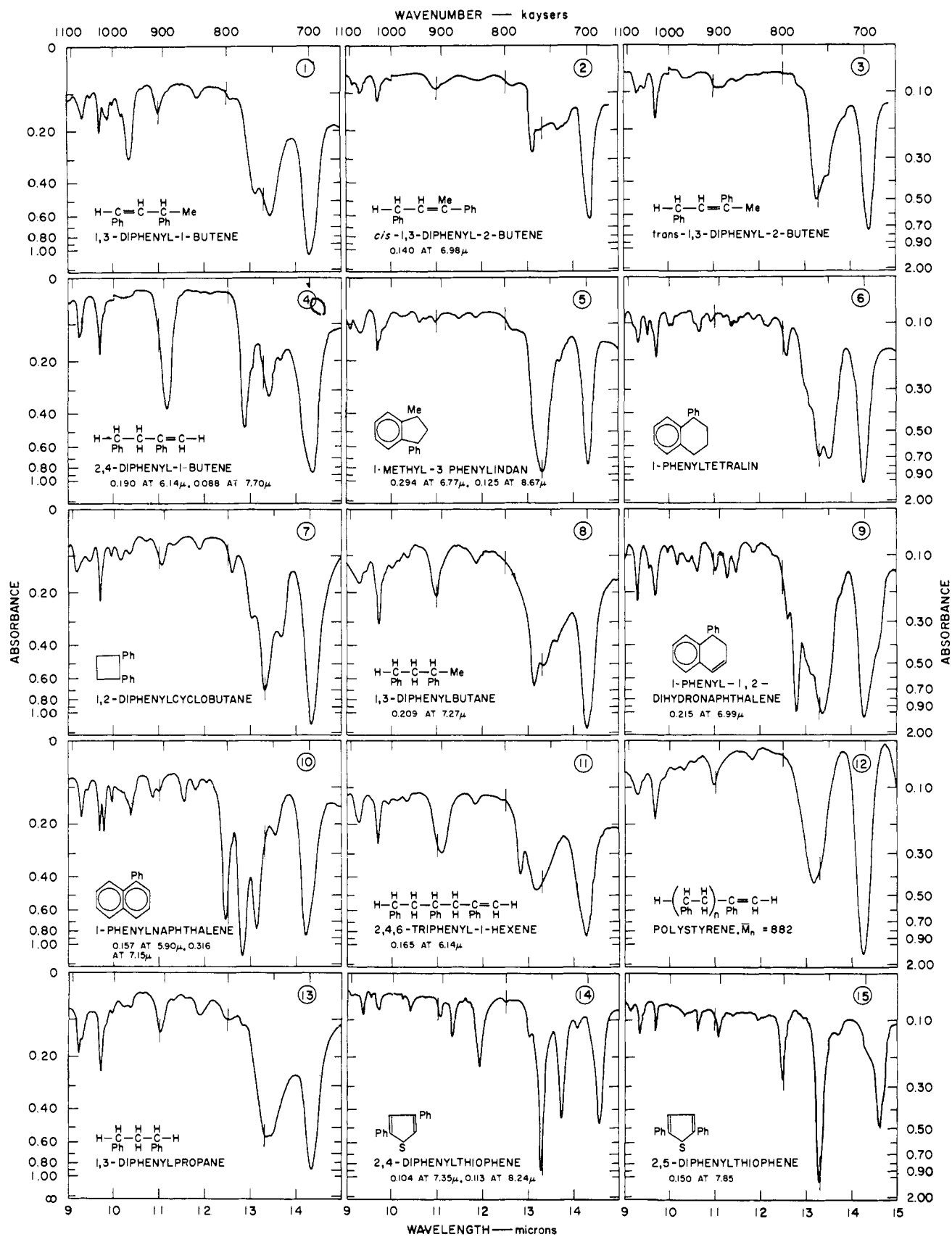(11) E. Baumann and E. Fromm, *Chem. Ber.*, 28, 890 (1895).

Figure 1. Infrared absorption spectra between salt plates and identifying numbers of styrene dimers and related compounds. Other distinctive bands and their maximum absorbances on the same sample are indicated. The curves are marked at 11.00, 12.50, and 13.30 μ to bring out differences at critical points. Glpc retention times for some of the compounds are: **2** and **13**, 10.5 min; **8**, 11.3 min; **4** and **5**, 13.3 min; **1**, 15.6 min; **7**, 16.1 min; **6**, 17.9 min; **3**, 18.6 min; **9**, 20.4 min; **10**, 26.0 min.

g of bromobenzene under a nitrogen atmosphere for 7 days at 158–159°. The product was then distilled at reduced pressure, finally to 100° residue temperature at 1 mm, leaving a residue

corresponding to 12% conversion of the styrene. Fresh styrene was added to the distillate to restore the original proportion of styrene and the experiment was repeated. From five such ex-

Table I. Dimerization of Styrene

Expt no.	Retarder or cat.[a]	Reaction time, hr	Conversion, %		Indicated compound[b] in dimer fraction, %										Footnote
			Dimer	Polymer	1	2	3	4	5	6	7	8	9	10	
Experiments without Solvent at 143–150°															
Ref 2	None (155°)	0.18	0.2	13.7											
23	2.0 TNB	15	2.8	39.1						5	38	7	28	22	c
36	2.0 TNB	15.1	1.7	46.6				11		9	61		13	4	c
25	2.0 PA	5.0	1.1	2.5						30	23		43	4	c
39	2.0 PA	15.2	1.9	12.8				4		18	25		42	11	c
21	0.10 I_2	25	11.2	53.3	?			?	1?	84	9?	3		3	d
24	0.10 I_2	25	9.4	54.6	3?					86	6?	3		2	e
14	0.50 I_2	40	19.0	58.2	3?					53	5?	15	6	18	
29	2.0 I_2	20	13.3	69.2					5	3	2	80		10	
31	2.0 I_2	20	11.0	72.2					10			78		10	
49	2.0 I_2	20	19.1	56.7	2				4			80		14	
34	0.31 S	3.0	3.8	36.8		2	6	69				9% 13		6% 15?	
40	0.31 S	3.0	4.0	48.4		~5	~30	~45				9% 13			f
44	0.31 S	1.5	0.7	13.4		3	12	36				12% 13		37% 15?	d,g
45	0.31 S	3.0	1.2	65[g]		1	4	53				20% 13		22% 15	d,g
Styrene Refluxed with Aqueous H_2SO_4 of Stated Strength[4]															
37	53%	4	>13	<47	71			7	22						
A1	53%} 62%}	4 / 13	77	6	10				90						
Exposed in Sealed, Evacuated Pyrex Tube at ~40° to Sunlight (expt 30) or Mercury Lamp															
30	0.10 I_2	60	0.49	0.34	10?					16	40?	28		5	h
32	0.10 I_2	90	<1.7	16	10?					30?	32?	28?			
46	10 BzPh	24	1.0	7.7				10?				90			d,i
47	10 BzPh 0.052 I_2	24	1.0	8.2				14?			86				d,i
50	11.7 AcPh	24	~0.1	2.5											
14.2 wt % Styrene (0.38% in B1–B5, 0.63% in B14) Refluxed in C_6H_5Br at 155–157°															
Ref 2	None	1.0	0.3	16.4											
27	2.0 TNB	24	1.9	8.0						33	23		19	25	c
28	2.0 PA	48	3.4	16.8						46	24		26	4	c
18	0.1 I_2	24	7.0	8.9	~10					~70	?				f
19	0.5 I_2	24	14.5	25.2				3		36	22	34		4	
20	2.0 I_2	5	4.4	19.5				4?	5	9	1	76		4	
42	0.31 S	3.9	0.73	6.9		~40, −60		<5		~5	~5	~10	~5% 15	~8	f
41	0.31 S	24.2	0.81	58.5		Mostly		<5		?	?	?		?	f
B1–B5	None	168	1.5	~12	?	0, −40		~15	~30	~10	0–20				
B14	t-Bu_2O_2	0.50	0.094	1.06				>90							c,f

a TNB, trinitrobenzene; PA, picric acid; quantities in wt % on styrene. b Key in Figure 1. c See Experimental Section for removal of by-products by chromatography, for formation of unknown compound from PA, and for analysis of dimer B14. d Dimer separated by precipitation of polymer. e 10.8% dimer and 53.2% polymer by precipitation of polymer; nearly all of 6 isolated by crystallization. f Analysis by ir instead of glpc. g Glpc on fluorosilicone column. Higher conversion to polymer in 45 is due to somewhat higher average temperature. h 50% 1 + 7. i BzPh partly separated from dimer by crystallization; M_n of polymer was 9200 and 8000 in expt 46 and 47.

periments, 10.9 g of residue was obtained; it was separated by distillation into 1.32 g of "dimer," 1.95 g of "trimer," and 7.36 of polymer. The "dimer" contained 10.5% bromine. The gas chromatogram was run too rapidly to give adequate resolution, and the dimer analysis in Table I is based on infrared absorption.

In expt B14, 3 l. of bromobenzene solution, 0.0787 M in styrene and 0.001 M in di-t-butyl peroxide at reflux temperature, were refluxed (157°) for 30 min under a nitrogen atmosphere. Then styrene and peroxide (92.4% and 18.3% calculated as remaining) were added to restore original concentrations and heating was continued for 30 min, and so on. After 12 heating periods (6 hr) the solution was distilled at reduced pressure, finally to 170° residue temperature at 1 mm (with no sign of distillation of dimer). The remaining 25.0 g of polymer was separated, by three precipitations from benzene with methanol, concentration of the solutions, and reprecipitation of the concentrate, into 3.4 g of soluble and 21.5 g of insoluble polymer. The soluble material was distilled at about 0.5 mm to give 0.28 g of dimer (bp 108–150°) and 1.43 g of residue. The dimer fraction contained 85.8% C, 7.51% H, and (by difference) 6.7% Br, mol wt 223. Its infrared absorption was very close to that of dimer 4 except for some weak absorptions at 5.90, 7.83, 9.97, 11.88, and 12.10 μ (perhaps due to benzaldehyde by oxidation); further, the absorption at 13.3 μ was as strong as at 12.86 μ. The fraction seems to be >90% 2,4-diphenyl-1-butene. The trimer fraction had a mol wt of 317 and a similar absorption (11), but lacked the absorptions in the impure dimer fraction at 5.90, 7.83, and 12.10 μ.

Disproportionation of Phenyltetralin and 1,3-Diphenyl-1-butene with Iodine. A mixture containing 1.05 g each of once-crystallized phenyltetralin (6) and of dimer 37 (66% 1) and 0.02 g of iodine was heated to 140° for 21 hr in a sealed, evacuated tube. Investigation of the product by glpc and infrared absorption showed that 1 had nearly disappeared, that much of the 6 had reacted, and that considerable 8 and 10 had been formed.

Results

Reaction Products. Ten C_{16} hydrocarbon products (1–10) and two diphenylthiophenes (14, 15) have been identified in the dimer fractions. The proportions of these have varied greatly with the experimental conditions. The key to the structures is in Figure 1, and the dimer compositions are in Table I.

The uncomplicated thermal reactions without solvent at 150° and in bromobenzene at 157° apparently yield mostly 1-phenyltetralin (6) and 1,2-diphenylcyclobutane (7), as shown by the TNB and PA runs. However, these nitro compounds effect some dehydrogenation of 6 to 9 and 10. After allowance for this reaction, about three times as much 6 as 7 is formed (expt 36 is an unexplained exception). Experiments B1–B5 are an effort to avoid inhibitors and to use dilution only to suppress polymerization. However, the long reaction time (1 week), and possibly traces of hydrogen bromide, led to quite a mixture of products, 5 being associated with acid catalysis[4] (expt A1 and 37). By procedure and infrared absorption the products of B1–B5 correspond to those reported previously.[2]

The photodimerization gives higher proportions of diphenylcyclobutane (7) and the benzophenone-sensitized dimerization gives this product almost exclusively, although very slowly. The presence of iodine in the photosensitized reaction had little effect on the rate or products; its steady-state concentration was probably very low. Acetophenone was ineffective as a sensitizer.

Iodine and sulfur had specific catalytic effects in dimerization, as well as retarding properties for polymerization of styrene. The effect of iodine, which varied with its concentration, will be brought out further in the Discussion. Sulfur (1 mol %, 0.31 wt %) was a poor retarder of polymerization but led to the formation of large proportions of 2,4-diphenyl-1
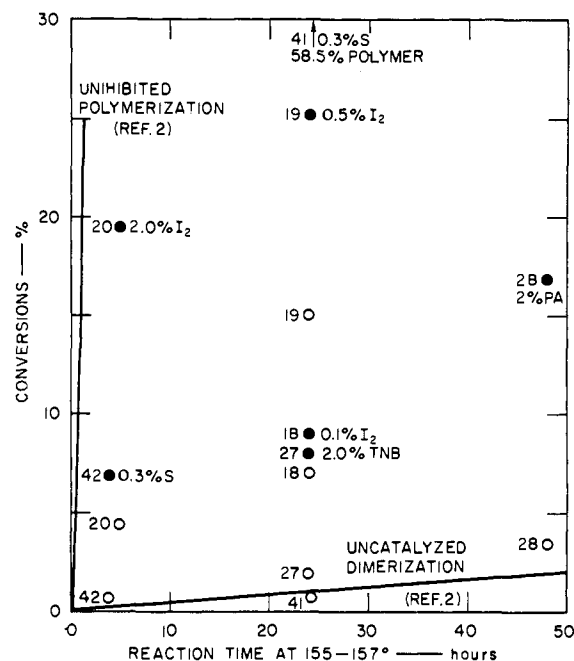

Figure 2. Yields of dimers (O) and polymers (●) on refluxing a 14.2% solution of styrene in bromobenzene.

butene (4) in the dimer fraction along with smaller proportions of the isomeric 2 and 3. In the slower reactions in bromobenzene solution, the proportions of these compounds were reversed, and other isomers and dehydrogenation products appeared. 1,2-Diphenylpropane (13) was recognized only in runs containing sulfur. At first we thought that it arose from cracking of polystyrene during separation by distillation[10] of the low yield of dimer from polymer. However, the appearance of even more 13 in expt 44 and 45, where most of the dimer was separated by precipitation of polymers, precludes this explanation. It may arise by random cracking of the polymer chain, the radical being formed by attack of sulfur and destroyed by transfer with SH groups. The structure of 15 suggests an origin by reaction of the diradical ·CHPhCH₂CH₂CHPh· or of the dimer 7 with sulfur. Product 14 was not recognized in any dimerization experiment, but was a major product of dehydrogenations by sulfur of open-chain dimers at 250–275°.

Rates of Dimerization and Polymerization. Experiments in refluxing bromobenzene, which are summarized in Figure 2, had good temperature control and can be compared directly with earlier uninhibited runs.[2] Amounts of inhibitors, by weight, based on styrene, are given near the solid circles for yields of polymers. Experiment numbers relate points for dimer yields (open or half-shaded circles) to points for polymer yields (shaded circles). The lowest rates of formation of dimer are found in the presence of picric acid and trinitrobenzene. These rates are close to the lower line, which represents the calculated rate of formation of styrene dimers[2] in the absence of both inhibitors and of high polymers. Dimer is formed considerably faster in the presence of iodine, and the more iodine that is present, the faster dimer is formed. For inhibiting formation of higher polymers, trinitrobenzene, picric acid, and 0.1% of iodine are equally effective, but larger quantities of iodine give increasing rates of polymeriza-
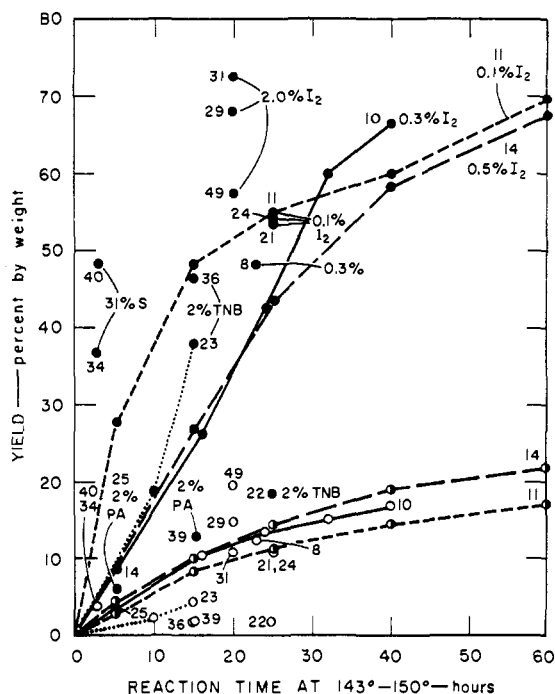
Figure 3. Yields of dimers (O and ◑) and polymers (●) on heating styrene at 143–150°.

tion. Apparently iodine is a very good inhibitor of free-radical polymerization, but high concentrations give some cationic polymerization, as suggested by Bartlett and co-workers.[12,13] The rate of the uninhibited polymerization[2] is indicated by the steeply rising line at the left.

Figure 3 summarizes rate data in the absence of a solvent. Here, temperature control was less satisfactory, but the pattern is the same. When more than one experimental point is available for one experiment, the points are joined by a line in this figure. Again the lowest rates of formation of both dimer and polymer are found in the presence of trinitrobenzene and picric acid. The highest rates are found in the presence of the most iodine, or in the presence of sulfur, which seems to be a poor retarder.

Discussion

As for our original objective, this work has shown that the dimer formed from sytrene at 150–160° is actually a complex mixture, often including hydrogenation and dehydrogenation products, with a composition depending on reaction conditions. The product formed by thermal reactions in refluxing bromobenzene[2] (expt B1–B5) is complicated further by acid catalysis, isomerization of primary products, and chain transfer with bromobenzene. The minute yield of dimer formed in a short time in the thermal polymerization of neat styrene[14] at 130° is much simpler (70% 6 and 15% 7). The reproducibility of our results with trinitrobenzene and picric acid probably depends on effects of decomposition products as catalysts and the fact that 7 is relatively unstable and formed reversibly.[7]

(12) D. S. Trifan and P. D. Bartlett, J. Amer. Chem. Soc., 81, 5573 (1959).
(13) G. Fraenkel and P. D. Bartlett, ibid., 81, 5582 (1959).
(14) K. F. Müller, Makromol. Chem., 79, 128 (1964).

The products of the simplest, nonradical, thermal processes correspond to both reactions

$$2C_6H_5CH=CH_2$$
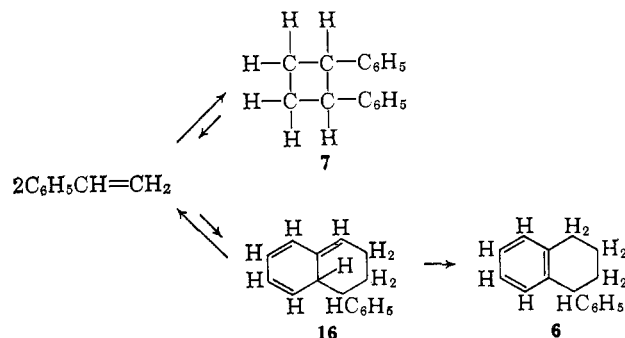
The first of these is promoted by light and especially by benzophenone as photosensitizer. The second is promoted by iodine and might also be promoted by base. Zwierzak and Pines[15] refluxed stabilized styrene with 2% of potassium t-butoxide for 24 hr and reported 98% of 6 in the dimer fraction, but no blank without base is cited and 70% of 6 has been reported under mild conditions.[14]

Formation of 6 and 7 is apparently accompanied by acid-catalyzed or radical chain reactions, often minor, leading to formation of compounds 2, 3, 4, and 5.

Effect of Iodine. Experiments at 150° in the presence of 0.1 wt % of iodine show that this agent retards polymerization of styrene but strongly and specifically accelerates the formation of 6. This result is readily rationalized by the last equation above if iodine (possibly hydrogen iodide) assists in the isomerization of the unstable Diels–Alder type of intermediate, 16, present only in very low concentration, to the product 6. Higher concentrations of iodine give rise to a faster polymerization; the formation of some dimers 1 and 5, associated with acid catalysis,[4] is consistent with the cationic mechanism suggested by Bartlett and co-workers.[12,13] The formation of the disproportionation products 8, 9, and 10 is also consistent with formation of 1 by acid catalysis and its iodine-catalyzed reaction with 6.

Mechanism of Thermal Initiation of Polymerization. After the postulation of 16 as an intermediate in the formation of 6, the next plausible step is to use the reaction

$$16 + C_8H_8 \longrightarrow \ + \ C_6H_5-CH-CH_3$$
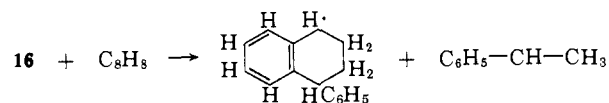
to account for the third-order initiation in the thermal polymerization of styrene in bromobenzene.[2] The third-order initiation is strongly supported by the work of Hiatt and Bartlett.[16] The involvement of o-hydrogen atoms is supported by the work of Kirchner.[17] The mechanism proposed above[1] has been cited by them and also by Dulog[18] and is consistent with the observed activation energy[1] of 29 kcal/mol. The objections of Burnett and Loan[19] do not apply to styrene.[20] The

(15) A. Zwierzak and H. Pines, J. Org. Chem., 28, 3392 (1963).
(16) R. R. Hiatt and P. D. Bartlett, J. Amer. Chem. Soc., 81, 1149 (1959).
(17) R. Kirchner, Makromol. Chem., 96, 179 (1966).
(18) L. Dulog, Chimia, 19, 158 (1965).
(19) G. M. Burnett and L. D. Loan, Trans. Faraday Soc., 51, 219 (1955). Their objection to the proposed over-all ⁵/₂ order for the

intermediate 16 has been proposed[14] as a regulator of molecular weight in the thermal polymerization of styrene, and one like 16 has been used to account for rate–molecular weight anomalies in the polymerization of o-chlorostyrene.[21]

If 16 reacts directly with diphenylpicrylhydrazyl, then the unexpectedly high rate of disappearance of this inhibitor in the thermal polymerization of styrene may be accounted for.[22,23]

Mechanism of Chain Transfer with Bromobenzene and Sulfur. The di-t-butyl peroxide initiated polymerization of styrene in bromobenzene (expt B14) shows that the dimeric chain-transfer product is almost entirely 2,4-diphenyl-1-butene (4), containing only a small proportion of bromine compounds or of bromobenzene residues. How do we account for a mathematically conventional effect of bromobenzene in reducing the molecular weight of polymerizing styrene,[2] without incorporation of (much) bromobenzene in the product, and with the formation (apparently) of the less stable oligomer with terminal $PhCH_2-$ and $=CH_2$ groups? The following proposal meets these requirements. The growing styrene chain adds to a "double bond" in the benzene ring and then continues to grow.
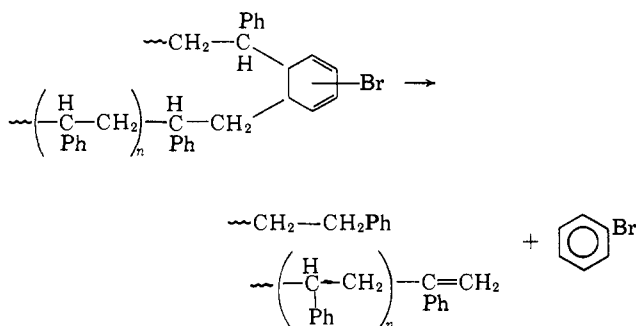
The indicated rearrangement of a hydrogen atom is sterically reasonable, but the value of n when rearrangement occurs is unknown. A similar hydrogen transfer has been proposed[24] for an initiation of styrene polymerization by t-butoxy radicals in bromobenzene.

Sulfur-retarded polymerizations give predominantly the same type of chain-transfer product. According to Bartlett and Trifan,[25] S_8 units appear first in the polystyrene. As they act as retarders, they are eventually converted into S_2 units. By analogy with the scheme above, some of those S_2 units may then be released, with formation of the appropriate end groups in the polymer.

Dimers Made with Metalloorganic Catalysts. Figure 4 shows matched gas chromatograms for dimers from expt 14 (with 0.5% iodine), and from three experiments

polymerization of styrene[2] does not fairly represent the data. A point-by-point determination of the order of the reaction for 0.05 to 0.015 M styrene in bromobenzene gives orders from 2.49 to 2.73 for the H fractions, with no trend with concentration.

(20) A. D. Jenkins, *ibid.*, **54**, 1885 (1958).

(21) O. F. Olaj, *Monatsh. Chem.*, **97**, 1437 (1966).

(22) K. E. Russell and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **75**, 502 (1953).

(23) W. A. Pryor, private communication, has suggested that both the rate of disappearance of diphenylpicrylhydrazyl and the rate of thermal initiation in the oxidation of styrene may measure the rate of formation of Diels–Alder adduct.

(24) D. B. Anderson, G. M. Burnett, and A. C. Gowan, *J. Polymer Sci.*, **A1**, 1465 (1963).

(25) P. D. Bartlett and D. S. Trifan, *ibid.*, **20**, 457 (1956).
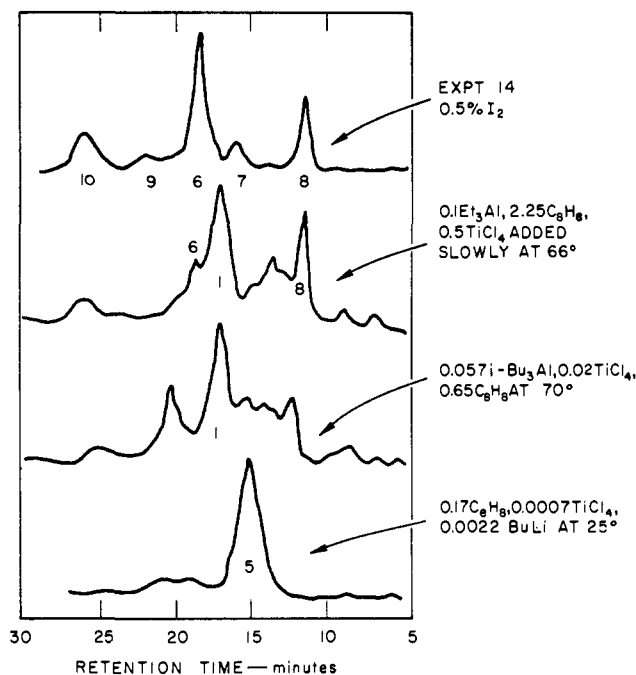
Figure 4. Matched gas chromatograms (at 235°) of dimer fractions. Legends indicate order of addition of reagents. Numbers are designations in Figure 1.

with metalloorganic catalysts. The aluminum–titanium catalysts gave some isotactic polystyrene; the lithium–titanium catalyst gave none. The fractions of dimer in the total polymer increased from 6% in the second experiment to 60% in the last. The principal dimer associated with the alkylaluminum catalysts was 1,3-diphenyl-1-butene (1), and with the lithium combination, 1-methyl-3-phenylindan (5). Both dimers are products of acid-catalyzed polymerizations. It may be significant that the indan, which requires stronger acid for its formation, was produced in the only experiment in which the titanium tetrachloride was added before the metal alkyl.

Of particular interest is the change in dimer patterns with the catalyst used. These changes suggest that comparison of dimer fractions may be a convenient means of comparing and standardizing metalloorganic catalysts.