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Heats of Polymerization. III. Styrene and Substituted Styrenes

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The apparatus and experimental procedures used in this research are the same as previously employed for investigations of the heats of polymerization of various esters of methacrylic acid.^{1,2} During the present investigation it was found that the vapor phase calorimeter showed a very small heat loss. This was not sufficiently great to affect seriously experiments wherein the polymerization was rapid, *e. g.*, the polymerization of methacrylic esters. However, the rate of polymerization of styrene, under the conditions employed, was sufficiently slow so that the heat loss had to be determined and a correction applied therefor. The substituted styrenes reported in this paper polymerized at rates exceeding that of styrene, and though in some cases the heat loss was not serious, we have corrected for it in all cases.

The apparent heat of polymerization of styrene and the substituted styrenes was found to be dependent upon the concentration of catalyst employed, so that the final values reported were corrected by extrapolation to zero catalyst concentration.

Experimental

Materials.—Styrene of commercial grade was vacuum-distilled and the distillate was washed with 10% sodium hydroxide to remove possible entrained inhibitor, dried with calcium chloride and again vacuum-distilled. Finally, it was partially crystallized twice at the temperature of Dry Ice, the uncrystallized portion being discarded. Bromination values agreed with the theoretical. The monomer was stored in Dry Ice until used.

Benzoyl peroxide was Eastman Kodak Co. white label grade.

Carbon tetrachloride and toluene used as heat-exchange liquids were purified as previously described.¹

Ethylvinylbenzene,³ containing a mixture of the isomeric forms, was shown to be 99.7% pure by bromine titration, *b. p.* 56° (5.4 mm.), *n*_D²⁵ 1.5331.

o-Chlorostyrene³ was found to be 99.98% pure by bromine titration and the freezing point of about -65° is in agreement with this conclusion, *b. p.* 187°, *n*_D²⁵ 1.5625, *d*₄²⁵ 1.09.

p-Chlorostyrene³ was 99.81% pure by freezing point determination, *m. p. ca.* -15°, *b. p.* 194°, *n*_D²⁵ 1.5634.

2,5-Dichlorostyrene was obtained by fractional distillation, under vacuum, of the commercial monomer. The distilled product was twice purified by slow cooling in an ice-bath until approximately 50% was crystallized, and discarding the liquid remaining. The recrystallized product melted at 8°. The position of the substituent halogen atoms was verified by potassium permanganate oxidation of the dichlorostyrene. The acid obtained melted at 154.5-155.5° (uncor.), which agrees with the reported value of 154° for 2,5-dichlorobenzoic acid.⁴ A

portion was converted to the 2,5-dichlorobenzamide which showed a melting point of 159-160°.^{5,6} Calcd. for C₇H₅-NOCl₂: N, 7.37. Found: N, 7.20.

Apparatus and Procedure.—Preliminary experiments indicated that residual monomeric styrene was present in the polymer, although heat evolution had apparently ceased. All polymers were analyzed for unreacted monomer by the bromination method of Uhrig and Levin,⁷ with the following modifications: After cooling, the reaction tube and the polymer were fragmented in a mortar, transferred to a 250-cc., glass-stoppered Erlenmeyer flask, and 20 cc. of chloroform was added. The polymer usually dissolved completely overnight. Fifty cc. of glacial acetic acid was slowly added to this solution, with constant agitation. Precipitation of the polymer occurred. The contents were titrated with 10% bromine solution in glacial acetic acid. Toward the end-point, the monomer was squeezed from the precipitated polystyrene by means of a stirring rod. The end-point was considered reached when one drop of bromine solution produced a color lasting over five minutes. In all polymerizations at 76.8°, bromine absorption never exceeded an amount corresponding to 2% of monomer initially present. The amount of residual monomer was lower with the higher catalyst concentrations. In all cases, the ΔH values were corrected for residual monomer. In the cases of substituted styrenes where the rates of bromination are slow, an excess of bromine was added and back-titrated with sodium thiosulfate solution, after allowing the mixtures to stand for the length of time necessary for complete bromination. These conditions were determined from control experiments with monomer alone.

The construction and operation of the calorimeter have been previously described.^{1,2} In order to calibrate the apparatus, the usual glass vial containing the sample to be polymerized was replaced by one similar in construction but containing a heating element made of 5 ohms of no. 30 Manganin wire and filled with liquid carbon tetrachloride as heat conductant. This assembly was immersed in carbon tetrachloride in the Dewar flask. Copper leads, sealed into the ends of the vial, extended above the opening of the calorimeter and were soldered to long, flexible multistrand leads of very fine copper wire. The leads were loosely held in a slightly sagged horizontal position by clamping the ends in two stationary binding posts to which the current and potentiometer leads were soldered. With the rest of the system suspended freely, the sensitivity of the scale was reduced slightly, owing to the rigidity of the leads. The weighings could, however, be reproduced to 0.01 g. if care was taken to ensure that the system was at a definite position at each weighing. On the outside of the Dewar tube near the opening, the wires were given a sharp U-shaped bend to provide a dropping point for condensation formed along the upper part of the wire. After the boiling became constant, the time required to vaporize a predetermined amount of carbon tetrachloride was determined. A Leeds and Northrup Type K Potentiometer was used to measure the potential across the heater at the position of the binding posts mentioned. The current was measured by the potential across a standard resistance in series with the heater. In the final calculations, corrections were made for the resistances of the leads above the liquid in the Dewar tube. The rate of vaporization of carbon tetrachloride was a linear function of the rate of heat input and the slope gave a calculated value of 46.8 for

(1) Tong and Kenyon, *THIS JOURNAL*, **67**, 1278 (1945).

(2) Tong and Kenyon, *ibid.*, **68**, 1355 (1946).

(3) These unsaturates and the physical constants quoted were very kindly supplied to us by the Dow Chemical Company, through the courtesy of Dr. L. R. Drake. The samples contained no inhibitor and were stored in Dry Ice until used.

(4) Crauw, *Rec. trav. chim.*, **50**, 773 (1931); Gassmann and Hartman, *THIS JOURNAL*, **63**, 2393 (1941).

(5) The previously reported value is 155°, Beilstein, *Ann.*, **179**, 290 (1875).

(6) We wish to thank Dr. J. H. Van Campen, of these Laboratories, for the chemical verification of this isomer.

(7) Uhrig and Levin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

the heat of vaporization of carbon tetrachloride in very good agreement with Mathews' value of 46.55 cal./g.⁸ However, the curve did not pass through the origin.

The deviation was presumably due to heat lost through the walls of the Dewar flask and therefore not used in vaporizing its equivalent amount of carbon tetrachloride. The constant rate of heat loss suggests that superheating is necessary to produce bubbles in the liquid and that it is quite insensitive to the rate of boiling for a given heater, container and liquid.

Results and Discussion

For brevity, we have included only two polymerization curves derived from photographic recordings which are typical of the results obtained and which illustrate (Fig. 1) the course of the polymerization under different reaction conditions. For the remainder of the runs, only the final values of apparent ΔH as kcal./mole of monomer are given in Table I.

TABLE I

HEATS OF POLYMERIZATION OF STYRENES AS FUNCTIONS OF TOTAL MONOMER USED AND CATALYST CONCENTRATIONS

Benzoyl-peroxide cat., mole %	Moles of monomer reacted $\times 10^3$	ΔW (g.)		$-\Delta H$ kcal./mole ^a (g. CCl ₄)	α (g. CCl ₄)	In-flection time, min., <i>i</i>	Const., <i>C_i</i>	D. P.
		Exptl.	Calcd.					
Styrene								
3.08	51.6	19.67	19.63					
	49.8	18.88	18.93					
	32.7	12.40	12.32	17.95	0.33	140	0.41	38
	17.4	6.25	6.40					
	13.2	4.80	4.81					
	8.6	3.11	3.00					
1.39	41.9	14.93	15.10					
	37.9	14.00	13.63					
	34.2	12.00	12.27	17.04	.29	205	.42	45
	17.0	6.11	5.95					
	8.7	2.85	2.91					
	8.2	2.73	2.72					
0.39	46.0	16.00	15.82					
	43.9	14.70	15.09					
	37.0	13.35	12.66	16.31	.35	365	.44	85
	35.8	11.70	12.24					
	26.2	8.97	8.87					
	12.2	3.94	3.94					
Ethylvinylbenzene								
.4	28.3	10.06		16.86	.23			
	5.8	1.88						
1.10	30.3	10.42		16.65	.46			
	5.4	1.48						
0.65	32.8	11.21		16.37	.37			
	10.7	3.41						
2,5-Dichlorostyrene								
.82	44.1	17.06	16.98					
	25.5	9.65	9.78	17.97	.10			
	2.9	1.08	1.02					
.64	41.7	15.61		17.39	-.01			
	3.2	1.19						
.48	45.2	16.73		17.27	.09			
	3.5	1.21						
.29	46.0	16.64		16.92	(0)			
.17	46.6	16.64	16.73					
	33.0	11.89	11.82	16.77	0.11			
	12.5	4.42	4.42					
	3.6	1.18	1.20					

(8) Mathews, THIS JOURNAL, 48, 562 (1926).

		o-Chlorostyrene				
1.15	36.0	13.54	13.53			
	8.9	3.27	3.27	17.56	.10	
	2.9	1.00	1.00			
0.48	48.3	17.57		16.89	(0)	
	.18	45.6	16.10	16.11		
.18	4.4	1.37	1.48	16.47	.08	
	3.5	1.28	1.16			
	.08	45.8	16.00	16.56	.35	
	5.5	1.61				
		p-Chlorostyrene				
1.55	47.2	17.82		17.52	(0)	
	1.08	38.7	14.17	17.16	.14	
.57	4.3	1.45				
	36.0	12.79		16.60	.09	
.39	3.7	1.23				
	46.3	16.15	16.27			
.39	42.2	14.90	14.84			
	15.5	5.51	5.51	16.21	-.10	
	7.3	2.60	2.65			
	3.2	1.29	1.22			

^a Calculated using 46.4 cal./g. as the heat of vaporization of carbon tetrachloride.^{1,2} Use of the observed value of 46.8 increases the $-\Delta H$ values by about 1%.

Experimentally, the ΔH measurements using styrene are more difficult to obtain than those of esters of methacrylic acid. This is chiefly due to the fact that styrene is less sensitive to the accelerating effect of benzoyl peroxide. If reaction is made to proceed at a reasonable rate in order to decrease errors due to heat leakage and drifts, a relatively large quantity of catalyst must be added, the presence of which increases the possibility of side reactions, as subsequently described. Experiments at higher temperatures introduce other more serious errors, for now, instead of a small constant rate at the beginning of the reaction, the polymerization proceeds with

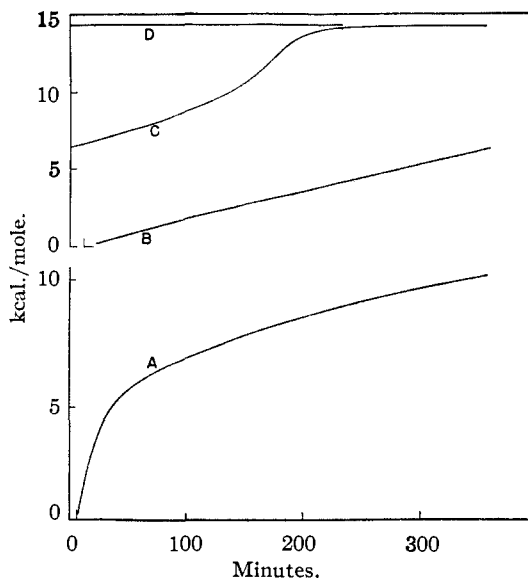


Fig. 1.—Polymerization of styrene (traced from photographic recordings): A, 110°, 0.066 mole per cent. catalyst; B, C, D, three sections of a continuous curve, 76.8°, 0.187 mole per cent. catalyst.

extreme rapidity and with changing rate. This makes extrapolation uncertain (compare Curves A and B, Fig. 1).

The correction for heat loss was obtained by polymerizing widely varying amounts of monomer at each catalyst concentration under investigation. If no heat loss occurs, a curve representing the amount of carbon tetrachloride vaporized as a function of monomer polymerized should be linear and, upon extrapolation, should pass through the origin. Represented in this manner (Fig. 2), the curve of the experimental data for styrene with 3.08 mole per cent. of benzoyl peroxide is linear but does not extrapolate to the origin. If we assume that, in polymerization experiments, heat loss takes place in the same manner as in the calibration experiments, then for a series of experiments using a given catalyst concentration, the heat loss in each case will be the same, since the duration of actual heat evolution is the same. This causes a parallel transposition of the theoretical linear weight loss-polymer relationship to the linear function of Fig. 2 with a negative intercept. The deviation (a) at the ordinate represents the correction for heat loss in terms of weight of heat-exchange liquid. This linearity is typical of the various monomers investigated at the catalyst concentrations shown in Table I.

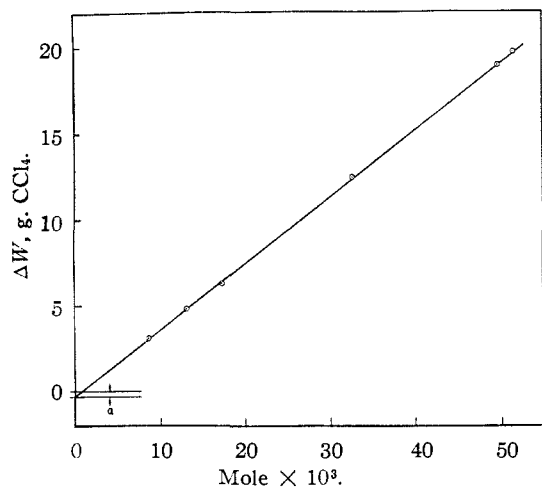


Fig. 2.—Weight of carbon tetrachloride vaporized vs. mole of styrene polymerized 76.8°, 3.08 mole per cent. catalyst.

The observed heat losses are tabulated in the sixth column of Table I. The loss, significant for ethylvinylbenzene and styrene, was very small for the halogenated styrenes because of their rapidity of polymerization. The fourth column, " ΔW , calcd.," gives the value calculated from the equation $46.4 (\Delta W + a) = n(-\Delta H)$ which corresponds to the best possible linear function drawn through the experimental data of column 3; hence the differences between columns 3 and 4 represent the scattering of the data from exact linearity. It will be seen that this is slight. The

fifth column shows the ΔH values calculated from the slopes of the experimental curves exemplified by Fig. 2, and hence are corrected for heat loss.

When the values for the apparent heats of polymerization of styrene and substituted styrenes (Table I) are plotted against the mole per cent. of benzoyl peroxide catalyst, a continuous variation is obtained, which, to the first approximation can be considered as a linear function (Fig. 3). The

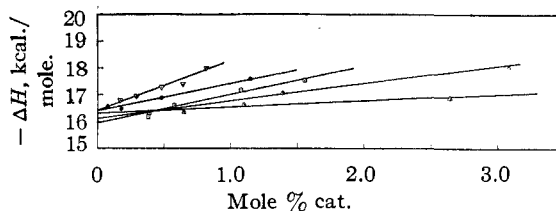


Fig. 3.—Heats of polymerization vs. catalyst concentration; 76.8°; ▽, 2,5-dichlorostyrene; ●, *o*-chlorostyrene; □, *p*-chlorostyrene; ○, styrene; △, ethylvinylbenzene.

average deviation from linearity is 1.5%. This dependence of ΔH upon catalyst concentration shows an apparent difference in the nature of the styrene polymerization as compared with that of the methacrylic esters. The latter showed no observable dependence upon catalyst concentration.² The dependence was greatest for dichlorostyrene, less for the monochlorostyrenes, still less for styrene, and least for ethylstyrene. This pattern parallels known inductive effects of halogen atoms and methyl groups leading to dynamic release of electrons in conjugate systems.³ Such electronic effects may well influence the behavior of the vinyl group of substituted styrenes, since this group is part of a conjugated system. Variations of ΔH with catalyst concentration can be explained if we assume a side reaction involving the benzoyl peroxide and some other components present. The most likely reaction is oxidation of the monomer by the benzoyl peroxide. The observations of other investigators suggest that such a reaction may occur under our experimental conditions. For example, Medvedev and Zeitlin¹⁰ showed that styrene can easily be oxidized by oxygen; Price and Tate,¹¹ and Bartlett and Cohen¹² showed that the rates of decomposition of substituted benzoyl peroxide and benzoyl peroxide, respectively, are several times greater in the presence of styrene. Brown¹³ showed that xylene can be oxidized when used as a solvent in the decomposition of benzoyl peroxide. It would be logical to assume that styrene, which is more easily oxidizable than xylene, might well be oxidized in the presence of large amounts of benzoyl peroxide to yield benzaldehyde and formaldehyde.

(9) J. R. Johnson, "Organic Chemistry," H. Gilman, editor, 2nd ed., John Wiley and Sons, New York, 1943, pp. 1821-1942.

(10) Medvedev and Zeitlin, *Acta Physicochim.*, U. R. S. S., **20**, 3 (1945).

(11) Price and Tate, *THIS JOURNAL*, **65**, 517 (1943).

(12) Bartlett and Cohen, *ibid.*, **65**, 543 (1943).

(13) Brown, *ibid.*, **62**, 2657 (1940).

Certain of the polystyrenes resulting from polymerization experiments with high catalyst concentrations were examined for aldehydes, using the bisulfite-iodine method. A certain amount of aldehyde was indicated but the quantity was not sufficient to account for the deviations observed. Possibly the aldehydes were further oxidized to benzoic and formic acids. On thermochemical grounds, it would appear that the deviations of ΔH with catalyst concentration are in excess of the benzoyl peroxide used. At present no better explanation is apparent.

The variation of ΔH with catalyst concentration does not seem to arise from double bonds at the end of the polystyrene chains. Unreacted bonds should be inversely proportional in number to the chain length. The molecular weights of the polystyrene samples decreased as the catalyst was increased; hence the observed ΔH should decrease with an increase of catalyst. The experiments of Table I show that the opposite effect was observed; *i. e.*, the apparent ΔH increased with catalyst concentration. If residual bonds were present in the polystyrene, they would very likely be determined during the bromine titration of excess monomer and thus corrected for. For purposes of future correlation, the degrees of polymerization calculated from viscosity measurements according to Kemp and Peters¹⁴ are recorded in Table I.

Despite the considerable (and varying) dependence of $-\Delta H$ of the various styrenes upon catalyst concentration, the curves of Fig. 3 extrapolate to about the same value at zero catalyst concentration, as shown in Table II. Though the

TABLE II

HEATS OF POLYMERIZATION AT 76.8° EXTRAPOLATED TO ZERO CATALYST CONCENTRATION

Monomer	$-\Delta H$, kcal./mole
Styrene	16.1 \pm 0.2
<i>o</i> -Chlorostyrene	16.4
<i>p</i> -Chlorostyrene	16.0
2,5-Dichlorostyrene	16.5
Ethylvinylbenzene	16.3

uncertainty factor of ± 0.2 kcal./mole is believed adequate for direct experimental values, it may be somewhat greater for extrapolated values. A value of 15.0 ± 0.47 kcal./mole has been directly determined¹⁵ for styrene and values of 13.8 to 10.6 kcal./mole are obtained from measurements of heats of combustion.¹⁶

Recently, the heat of polymerization of styrene

(14) Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1079 (1942).

(15) Goldfinger, Josefowitz and Mark, *THIS JOURNAL*, **65**, 432 (1943).

(16) Luschinsky, *Z. physik. Chem.*, **A182**, 384 (1938).

at 25° to form a solution of polymer in monomer was found to be¹⁷ 17.2 kcal./mole of styrene unit reacted. Subsequently, the heat of solution of polystyrene in monomer at 25° was determined¹⁸ as 0.86 ± 0.06 kcal./mole which, subtracted from the heat of partial polymerization, produces a $-\Delta H$ value for polymerization of 16.34 kcal./mole. These latter investigators measured the heats of combustion of styrene and of polystyrenes of two degrees of polymerization. From these data a heat of polymerization of 16.68 kcal./mole at 25° was calculated. Our value of 16.1 is in good agreement with the value of Brickwedde, though the temperatures of determination are different.

The relation between the time, t_i , of the first inflection of the recorded heat evolution curves (Fig. 1, B, C, D) and catalyst concentration, $cat.$, is $t_i = 100/(C_i\sqrt{cat.})$, where C_i is a constant (Table I) at an approximate average value of 0.42. This indicates that the reaction follows the same course with different amounts of catalyst. Other investigators have shown that the initial slope of the rate curve is proportional to the square root of the catalyst concentration.

The ΔH values for styrene at 110° (boiling point of toluene) have large experimental errors, due to difficulties of extrapolation, as mentioned before. Curve A, Fig. 1 represents a typical course of reaction, and at this temperature curves have no inflection points.

Summary

1. The isothermal calorimeter exhibits a small heat loss which becomes significant when monomers that polymerize slowly are under investigation. A method of determining and correcting for the heat loss is described.

2. The apparent heats of polymerization of styrene and substituted styrenes were measured and found to increase linearly with the catalyst concentration.

3. Extrapolation of the apparent heat of polymerization-catalyst concentration curves to zero catalyst concentration gave the following values of $-\Delta H$ as kcal./mole at 76.8°: styrene, 16.1, *o*-chlorostyrene, 16.4, *p*-chlorostyrene, 16.0, 2,5-dichlorostyrene, 16.5, ethylvinylbenzene, 16.3.

4. The dependence of $-\Delta H$ upon catalyst concentration is suggested as due to unknown side reactions, possibly that of oxidation.

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(17) Brickwedde, Division of Physical and Inorganic Chemistry, Atlantic City Meeting of the American Chemical Society, April, 1946.

(18) Roberts, Walton and Jessup, Division of Physical and Inorganic Chemistry, Chicago, Illinois, Meeting of the American Chemical Society, September, 1946.