those cationic dyes which do not conform to Beer's law in aqueous solution. Usually the silicates increase the relative intensity of the low wave length or β band, broaden it and displace this band toward even shorter wave lengths. The changes are not due to the alkalinity of the silicates. They are attributed to interaction, probably involving both electrostatic and van der Waals forces, of a dimeric or polymeric form of the dye with the oppositely charged silicate micelles.

The addition of sodium chloride, sulfate or trisodium phosphate decreases the interaction of the dye, pinacyanol chloride, and silicate. This effect of salts is not due entirely to the ionic strength of the solution.

Sodium silicates of different silica to alkali ratio have widely varying effects on the absorption spectra of pinacyanol chloride even when the silica concentration is the same.

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[CONTRIBUTION NO. 75 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Transfer in the Polymerization of Styrene. IV. The Effect of Chain Length on the Reaction of Styrene and Carbon Tetrachloride

BY FRANK R. MAYO

The first paper of this series,[1] on the basis of literature data, indicated the existence of a quantitative relation between solvent:monomer ratio in a reaction mixture and the solvent fragment content of the polymer. Work was at once undertaken to determine the limitations of this relation and its applicability to the preparation of very low molecular weight compounds. Breitenbach and Maschin[2] had previously obtained fractions containing as much as 22% chlorine, and Kharasch and co-workers have recently reported a polymer containing 7.6% chlorine,[3a] but only by the use of the more reactive bromotrichloromethane instead of carbon tetrachloride has a 1:1 product been isolated.[3b] These products are mixtures of compounds of the type, $Cl_3C-(CH_2-CHC_6H_5)_n-Cl$(or Br). The second paper[4] in this series showed that both the over-all second order rate constant and the transfer constant for the polymerization of styrene in carbon tetrachloride are independent (at low conversions and within experimental error) of average polymer chain lengths ranging from about one hundred to many thousands. It follows that either all the individual rate constants in the polymerization (initiation, growth, transfer, termination) are independent of chain length, as has been commonly assumed, or else there is mutual compensation of trends. In the present extension of the above studies to the very low molecular weight range, the ratio of the rate constants for chain growth and chain termination is found to vary little, if at all, as the average number of styrene units in the growing free radical decreases from twenty to two. On the other hand, the ratio of the rate constants for chain transfer with carbon tetrachloride and for chain growth of the radical, $Cl_3C-(CH_2-CH_6H_5)_n\cdot$, increases markedly with chain length as n increases from one to three, then remains constant to the largest values of n found.

Equations.—All the reactions considered between the peroxide catalyst (Cat.), monomer (M), and solvent (S) are represented by the following equations, where Cat.: represents radical from the catalyst, M· represents the free radical formed by the addition of any radical to a monomer, and S· is the radical formed by removal of an atom from the solvent by chain transfer. In this paper S· is $Cl_3C\cdot$ as shown by identification of disproportionation and coupling products of the radical containing one styrene unit.

$$\text{Cat.} \longrightarrow 2\ \text{Cat.}\cdot \qquad (1)$$

$$2\ \text{Cat.}\cdot \longrightarrow \text{products (first order combination)} \qquad (1a)$$

$$\text{Cat.}\cdot + \text{M} \longrightarrow \text{M}\cdot \qquad (2)$$

$$\text{Cat.}\cdot + \text{S} \longrightarrow \text{S}\cdot \qquad (2a)$$

$$\text{M}\cdot + \text{M} \longrightarrow \text{M}\cdot \qquad (3)$$

$$\text{M}\cdot + \text{S} \longrightarrow \text{S}\cdot \qquad (4)$$

$$\text{S}\cdot + \text{M} \longrightarrow \text{M}\cdot \qquad (5)$$

$$2\text{M}\cdot \longrightarrow \text{products} \qquad (6)$$

$$2\text{S}\cdot \longrightarrow \text{products} \qquad (6a)$$

When the kinetic chains are long (and the contribution of chain initiation and termination to the composition of the product can be neglected) and when essentially all polymer chains end by transfer

$$\frac{d[\text{M}]}{d[\text{S}]} = \frac{k_3[\text{M}\cdot][\text{M}] + k_5[\text{S}\cdot][\text{M}]}{k_4[\text{M}\cdot][\text{S}]} \qquad (7)$$

Since $k_4[\text{M}\cdot]\,[\text{S}] = k_5[\text{S}\cdot]\,[\text{M}]$ and since the transfer constant, C, is defined as k_4/k_3[5]

$$\frac{d[\text{M}]}{d[\text{S}]} = \frac{[\text{M}]}{\text{C}[\text{S}]} + 1 \qquad (8)$$

In the previous papers this 1 term has been neg-

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[1] Mayo, This Journal, **65**, 2324 (1943).

[2] Breitenbach and Maschin, *Z. physik. Chem.*, **187A**, 175 (1940).

[3] (a) Kharasch, Jensen and Urry, This Journal, **69**, 1100 (1947); (b) Kharasch, Reinmuth and Urry, *ibid.*, 1105.

[4] Gregg and Mayo, *ibid.*, **70**, 2373 (1948). Paper III, on transfer with hydrocarbons, will appear shortly in *Trans. Faraday Soc.*

[5] This equation is identical in form with the differential equation for the copolymerization of the monomers M_1 and M_2 when the monomer reactivity ratio of $M_2\cdot = 0$ and the monomer reactivity ratio of $M_1\cdot$ is $1/C$; *cf.* Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).

lected because it is small compared with the other terms, but for low molecular weight products, this term is essential if Equation (8) is not to predict the formation of products averaging less than one monomer unit per solvent molecule. In some cases, it is convenient to assume that all radicals containing x or fewer monomer units can grow but not transfer; the 1 in Equation (8) is then replaced by $x + 1$. In order to cover a wide range of ratios, this equation, in Fig. 1 and the discussion, has been used in the form

$$\log\left(\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{S}]} - 1 - x\right) = \log([\mathrm{M}]/[\mathrm{S}]) - \log C \quad (9)$$

Since this paper deals with the concept of a transfer "constant" which may depend on the number of units, n, in the growing radical, $M_n\cdot$, these individual "constants" are defined and determined by the relation

$$C_n = k_{4n}/k_{3n} = \frac{[\mathrm{M}]\,(\text{moles product with only } n \text{ M units})}{[\mathrm{S}]\,(\text{moles product with} > n \text{ M units})} \quad (10)$$

We shall consider next the effects of reagent concentrations on the rate of reaction of monomer and solvent. The efficiency with which catalyst fragments start chains will depend on the ability of the reaction medium to react with the radicals before they combine. According to the principles given by Matheson,[6] the fraction of catalyst radicals which start chains, F, is given by

$$F = \frac{k_2[\mathrm{M}] + k_{2a}[\mathrm{S}]}{2k_{1a} + k_2[\mathrm{M}] + k_{2a}[\mathrm{S}]} \quad (11)$$

If it is assumed that all chains end by reaction (6), so that $k_{6a} = 0$, then

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{Cat.}]} = 2F + (k_3[\mathrm{M}] + k_4[\mathrm{S}])\sqrt{\frac{F}{k_1k_6[\mathrm{Cat.}]}} \quad (12)$$

$$\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}[\mathrm{Cat.}]} = \frac{2k_{2a}[\mathrm{S}]}{2k_{1a} + k_2[\mathrm{M}] + k_{2a}[\mathrm{S}]} + k_4[\mathrm{S}]\sqrt{\frac{F}{k_1k_6[\mathrm{Cat.}]}} \quad (13)$$

If it is assumed that all chains end by reaction (6a) so that $k_6 = 0$, then

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{Cat.}]} = \left(\frac{k_3[\mathrm{M}]}{k_4[\mathrm{S}]} + 1\right)\left(\frac{2k_2[\mathrm{M}]}{2k_{1a} + k_2[\mathrm{M}] + k_{2a}[\mathrm{S}]} + k_5[\mathrm{M}]\sqrt{\frac{F}{k_1k_{6a}[\mathrm{Cat.}]}}\right) \quad (14)$$

$$\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}[\mathrm{Cat.}]} = 2F + k_5[\mathrm{M}]\sqrt{\frac{F}{k_1k_{6a}[\mathrm{Cat.}]}} \quad (15)$$

In all the experiments discussed in this paper, the proportions of styrene and carbon tetrachloride reacting were kept low enough so their concentrations may be considered as constant at the means of their respective initial and final concentrations, but all experiments were carried out to complete decomposition of the peroxide catalyst. Accordingly, Equations (12)–(15) have been integrated as if only the catalyst concentration changed, from an initial $[\mathrm{Cat.}]_0$ to zero. $-\mathrm{d}[\mathrm{Cat.}]/[\mathrm{Cat.}]^{1/2}$ then becomes $2[\mathrm{Cat.}]_0^{1/2}$. If we make the further simplifying assumption that the monomer and solvent consumed by direct action of the catalyst (reactions 2, 2a) can be neglected in comparison with the total solvent and monomer consumed, and since, by Equations (7) and (8), $k_3[\mathrm{M}] + k_4[\mathrm{S}]$ in Equation (12) may be replaced by $k_3[\mathrm{M}]\,\mathrm{d}[\mathrm{M}]/(\mathrm{d}[\mathrm{M}] - \mathrm{d}[\mathrm{S}])$, Equations (12) and (13) become, respectively

$$\frac{-\Delta[\mathrm{M}] + \Delta[\mathrm{S}]}{[\mathrm{M}]} = 2k_3\left(\frac{\mathrm{F}[\mathrm{Cat.}]_0}{k_1k_6}\right)^{1/2} \quad (16)$$

$$\frac{-\Delta[\mathrm{S}]}{[\mathrm{S}]} = 2k_4\left(\frac{F[\mathrm{Cat.}]_0}{k_1k_6}\right)^{1/2} \quad (17)$$

Replacing $(k_3[\mathrm{M}]/k_4[\mathrm{S}]) + 1$ in (14) by $\mathrm{d}[\mathrm{M}]/\mathrm{d}[\mathrm{S}]$ (Equation 8), both (14) and (15) become

$$\frac{-\Delta[\mathrm{S}]}{[\mathrm{M}]} = 2k_5\left(\frac{F[\mathrm{Cat.}]_0}{k_1k_{6a}}\right)^{1/2} \quad (18)$$

The following relations have also been used in the course of this work. The integrated form of equation (8) is

$$\log\frac{[\mathrm{S}_0]}{[\mathrm{S}]} = \frac{C}{1-C}\log\frac{\frac{1-C}{C}\frac{[\mathrm{M}_0]}{[\mathrm{S}_0]} + 1}{\frac{1-C}{C}\frac{[\mathrm{M}]}{[\mathrm{S}]} + 1} \quad (19)$$

the final 1's being replaced by $x + 1$ when radicals containing x or fewer monomer units do not transfer.

If the radical $M_1\cdot$ has a transfer constant, C_1, $\mathrm{M}_2\cdot$ has the transfer constant, C_2, $\mathrm{M}_3\cdot$ has the transfer constant C_3, and all longer radicals have the same transfer constant, C, then

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{S}]} - 1 = \frac{1 + \frac{[\mathrm{M}]}{C[\mathrm{S}]} + \left(\frac{C_3[\mathrm{S}]}{[\mathrm{M}]} + 1\right)\left(\frac{C_2[\mathrm{S}]}{[\mathrm{M}]} + 2\right)}{\left(\frac{C_1[\mathrm{S}]}{[\mathrm{M}]} + 1\right)\left(\frac{C_2[\mathrm{S}]}{[\mathrm{M}]} + 1\right)\left(\frac{C_3[\mathrm{S}]}{[\mathrm{M}]} + 1\right)} \quad (20)$$

When $C_3 = C$, (20) reduces to

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{S}]} - 1 = \frac{2 + \frac{[\mathrm{M}]}{C[\mathrm{S}]} + \frac{C_2[\mathrm{S}]}{[\mathrm{M}]}}{\left(\frac{C_1[\mathrm{S}]}{[\mathrm{M}]} + 1\right)\left(\frac{C_2[\mathrm{S}]}{[\mathrm{M}]} + 1\right)} \quad (21)$$

and, when $C_3 = C_2 = C$, to

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{S}]} - 1 = \frac{1 + \frac{[\mathrm{M}]}{C[\mathrm{S}]}}{\frac{C_1[\mathrm{S}]}{[\mathrm{M}]} + 1} \quad (22)$$

Experimental

Procedure.—Reagent carbon tetrachloride was used without purification. Purified styrene from the Dow Chemical Co. was distilled under reduced pressure and used at once, or (Expts. 19–22) stored at 5° and found free from polymer when used. Experiments containing more than 1 mole of carbon tetrachloride were refluxed. A nitrogen atmosphere was maintained in the apparatus in Expts. 21, 22, 29, 30 and 41, the only effect being a possible slight increase in rate of reaction. Heating was continued until the decomposition of the catalyst was complete, titration indicating 99% decomposition in forty-eight hours in a 100:1 carbon tetrachloride:styrene mixture.[7] The re-

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[6] Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

[7] Nozaki and Bartlett, This Journal, **68**, 1686 (1946), found that benzoyl peroxide was 40% decomposed in four hours at 80° in carbon tetrachloride.

action mixtures were then concentrated to a small volume under a Vigreux column at reduced pressure, keeping the liquid temperature below 40° to minimize polymerization of the styrene. These products, being liquid (at least when hot), were simply heated at 5 mm. pressure to a pot temperature of 125° or a vapor temperature of about 100° (no actual distillation taking place). The residues were weighed in the flask and then analyzed for chlorine.

Runs containing 1 mole or less of carbon tetrachloride were sealed off in evacuated tubes and heated in a bath of refluxing carbon tetrachloride. The products were precipitated from benzene with methanol, the residues being washed thoroughly with methanol. The liquors and washings were then concentrated to dryness at reduced pressure, and the small residues were combined with the precipitated polymers which were then isolated by the frozen benzene technique.[8]

TABLE I

EXPERIMENTAL DATA ON THE POLYMERIZATION OF STYRENE IN CARBON TETRACHLORIDE AT 76°

Expt.	Feed in moles C_8H_8	CCl_4	Bz_2O_2 ($\times 10^3$)	Time, hr.	Product g.	% Cl	C_8H_8 reacted, %
40	0.1893	0.1993	None	96	4.86	1.87, 1.81	24.2
39	.1893	.1992	None	96	4.96	1.97, 2.00	24.6
43	.200	.200	None	90	5.18	1.72, 1.75	24.4
42	.200	.400	None	192	6.73	3.16, 3.16	31.2
24	.200	1.000	0.005	88	2.69	6.43, 6.46 6.50, 6.50	12.0
29	.200	2.00	.020	87	3.51	10.87, 10.85	14.9
17	.250	5.12	.0625	48	3.84	15.25, 15.36	12.3
20	.250	5.00	.125	119	5.60	14.39, 14.49	18.0
30	.200	5.00	.100	87	4.42	17.85, 17.73	17.1
19	.200	20.0	.500	122	5.52	26.69, 26.61	18.5
22	.200	20.0	.500	93	5.57	26.99, 27.07	18.1
18	.100	40.0	.500	112	2.35	34.28, 34.30	13.5
21	.100	40.0	.500	134	3.05	33.47, 33.37	18.1
41	.100	40.0	.500	192	3.62	35.27, 35.20	20.8

TABLE II

CALCULATIONS FROM DATA IN TABLE I[a]

Expt.	(M/S)av.	$\Delta M/\Delta S$ unc.	cor.[b]	k^d liters moles^{-1} hour^{-1}	$\frac{-\Delta M + \Delta S}{M[\text{Cat.}]_0^{1/2}}$ uncor.	cor.[e]	$\frac{-\Delta S}{S[\text{Cat.}]_0^{1/2}}$ uncor.	cor.[e]	$\frac{-\Delta S}{M[\text{Cat.}]_0^{1/2}}$ uncor.	cor.[e]	Cav.
40	0.836	72.5[c]		0.00071							0.0117
39	.835	66.0[c]		.00073							.0128
43	.878	77.0[c]		.00074							.0115
42	.422	41.78[c]		.00073							.0104
24	.1880	19.53	19.44	(.00093)	18.9	3.6	0.191	.037	1.02	0.20	.0102
29	.0926	11.06	10.97	(.0022)	15.2	9.6	.140	.088	1.51	.95	.0092
17	.0459	7.41	7.20	(.0062)	10.4	9.8	.075	.065	1.63	1.42	.0073
20	.0455	7.92	7.76	(.0038)	11.1	8.6	.073	.056	1.61	1.24	.0067
30	.0366	6.19	6.08	(.0054)	11.2	9.6	.079	.067	2.16	1.84	.0060
19	.00907	3.60	3.43		9.3	8.9	.0323	.0307	3.55	3.38	.0036
22	.00907	3.49	3.34		9.2	8.9	.0333	.0321	3.68	3.54	.0038
18	.00233	2.38	2.19		7.5	7.4	.0126	.0124	5.38	5.30	.0018
21	.00227	2.52	2.36		10.6	10.5	.0159	.0157	6.96	6.87	.0016
41	.00224	2.31	2.19		11.65	11.5	.0199	.0196	8.38	8.77	.0018

[a] M, S, $-\Delta M$ and $-\Delta S$, the average quantities of monomer and solvent in the feed, and the amounts reacting, are given in moles, corrections to moles/liter cancelling out in the ratios used. The initial concentration of catalyst $[\text{Cat.}]_0$ is expressed in moles/liter of reaction mixture at about 25°, the volumes being calculated from the densities of reactants. [b] All calculations assume that 55% by weight of the catalyst appears in the reaction product. The corrected values (b) assume further that one additional molecule of carbon tetrachloride should appear in the product for each mole of catalyst initially used. Uncorrected values of ΔS used in columns to right. [c] No catalyst added. [d] Defined by the equation: $-d[M]/dt = k[M]^2$. [e] Uncorrected value × (% observed reaction − % uncatalyzed reaction)/% observed reaction.

To determine the importance of any uncatalyzed polymerization or reaction during concentration, a mixture of 0.20 mole styrene and 20 moles carbon tetrachloride was refluxed in contact with air for seventy-two hours, and then concentrated to 190 g. in four hours at atmospheric pressure under a Vigreux column, then at reduced pressure as described above. The residue weighed 0.50 g. and contained 20.6% chlorine and 1.8% of the original styrene. The chlorine content indicates that perhaps 1.5% of the original styrene reacted during refluxing, the rest during concentration at atmospheric pressure. This result led to concentrations at reduced pressure in the experiments here recorded.

Catalyst Residues.—The following experiments at a carbon tetrachloride:styrene ratio of 100:1 indicate the effects of benzoyl peroxide on the compositions of the products, from which free benzoic acid could be obtained by cold alkali extraction. Two reaction products from feeds containing 10 and 2 mole % of catalyst (based on the styrene), yielded 7.1 and 5.2% of the original weight of catalyst as benzoic acid. In another experiment, with 5 mole % catalyst, the whole product was heated to distill as much as possible, finally to 245° at 3 mm. pressure where loss of hydrogen chloride became rapid. This distillate contained 19.3 wt. % of the original catalyst as benzoic acid, showing partial cracking of benzoic esters. In three experiments the unreacted styrene was recovered and determined quantitatively, by index of refraction, in a concentrate with carbon tetrachloride. The weights and chlorine contents of the reaction products showed that they must contain 58.7% and 54.7% by weight of the original catalyst when the molar feed ratio of carbon tetrachloride:styrene:benzoyl peroxide was 1000:10:1, 51.5% from a 10000:50:1 feed. On the basis of these results, all calculations in Tables I and II assume that the reaction products contain residues from the catalyst amounting to 55% of its original weight.

Investigation of Reaction Products.—Table I lists all of the experimental data to be considered later. Two other experiments, started with a molar carbon tetrachloride: styrene:benzoyl peroxide ratio of 100:1.0:0.1 gave higher conversion of the styrene and the combined products were investigated carefully: 36.6 g. of product containing 32.25% chlorine, after two distillations at reduced pressure, gave 2.2 g. of a fraction boiling mostly at 110–130° and 11.5 g. of a fraction boiling mostly at 190–210°, both at 5 mm. pressure, the remainder being mostly undistillable; 1.56 g. of the lower fraction, containing 40.3% chlo-

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(8) Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

rine, was hydrolyzed by refluxing for a few minutes with 0.31 g. of potassium hydroxide in alcohol. The resulting allylic halide was separated from potassium chloride and alcohol and then refluxed for sixteen hours with an excess of silver nitrate in 50% alcohol.[9] The dark and gummy acids were distilled *in vacuo* and recrystallized several times from ligroin, yielding (1) 4–5 mg. of cinnamic acid, m. p. 130–130.5° (m. p. known cinnamic acid taken simultaneously, 131–2°; mixed m. p. 131–131.5°), neutral equivalent, 145 ± 5, (2) 0.0513 g. of acids, m. p. 107–113°, neutral equivalent, 152, and (3) 0.1109 g. of acids, m. p. 55–75°, neutral equivalent, 151. These acids therefore consist of cinnamic acid plus other acids of about the same neutral equivalent. Since three slow distillations of the lower melting fraction did not change the melting point significantly, the absence of *cis*-cinnamic acid is indicated. The 0.0678 g. of low-melting crystalline acids recovered had a neutral equivalent of 139. X-Ray diffraction studies by Dr. H. N. Campbell of this Laboratory proved the presence of crystals of benzoic and β-phenylpropionic acids, but showed no crystals of cinnamic acid. The presence of β-phenylpropionic acid as well as cinnamic acid in the original hydrolyzed product suggests that the 110–130° fraction may contain both 1-phenyl-3,3,3-trichloro-propene (48.05% Cl) and -propane (47.60% Cl) formed from *disproportionation* of $\mathrm{Cl_3{-}C{-}CH_2{-}\underset{\bullet}{C}HC_6H_5}$ radicals. The question of whether this fraction contains appreciable 1-phenyl-1,3,3,3-tetrachloropropane (54.95% Cl) is unsettled.

The 190–210° fraction contained 35.1% chlorine and must have contained the 2:1 reaction product (39.17% Cl). On standing at room temperature for a few weeks, this fraction began to deposit white crystals, and in the course of a few days, crude crystals amounting to 7.65% by weight of the fraction were collected on a filter. After recrystallization from alcohol, the crystalline material melted at 176–177° (cor.) This product was *meso*-1,1,1,6,-6,6-hexachloro-3,4-diphenylhexane, presumably formed by the *coupling* of two $\mathrm{Cl_3C{-}CH_2{-}\underset{\bullet}{C}HC_6H_5}$ radicals, in a yield of 0.036 mole per mole of benzoyl peroxide used initially.

Anal. Calcd. for $C_{18}H_{16}Cl_6$: Cl, 47.79. Found: Cl, 47.65.

This hexachloride was treated with a slight excess of silver nitrate in 70% alcohol for a few hours at 100°, yielding *meso*-β,β′-diphenyladipic acid, m. p. 270° (cor.), m. p. methyl ester 174° (cor.). The recorded[10] melting points of the acid and ester are 270° and 175°, respectively.

Discussion

Selection of Experiments.—More than forty experiments were carried out. The discussion will be based on the data in Table II, all of which are calculated from those in Table I. In reaction products containing 1.5–2.0% chlorine (from 1:1 feeds), the chlorine analyses in this paper are not usually reliable to better than 0.1%, as shown by analyses of known polymers with similar chlorine contents. In this range, reproducibility seems subject principally to analytical limitations and all experiments not known to be faulty are listed. In experiments with higher proportions of carbon tetrachloride in the feed, where duplicate experiments gave products of different chlorine contents, the high chlorine experiments are considered more reliable since all experimental errors (except in actual analyses for chlorine) tend to give low results: any polymerization during concentration, any styrene monomer not removed, any 1:1 reaction product lost in distillation, any loss of hydrogen chloride by product, any adsorption of oxygen during reaction, any hydrolysis by incidental moisture.

Calculation of C_n for $n \geq 4$.—This and succeeding sections are concerned with the behavior of the individual radicals, $\mathrm{Cl_3C{-}(CH_2{-}CH{-}C_6H_5)}_{n\cdot\,\mathrm{or}\,x}$, with carbon tetrachloride where n indicates the number of monomer units in the radical for which a transfer constant, C_n (Equation 10), is being considered and where radicals containing x or fewer monomer units do not transfer appreciably with carbon tetrachloride. Using data in Table II, Fig. 1 shows how the styrene–carbon tetrachloride ratio in the reaction product formed at 76°, $(\Delta M/\Delta S) - 1$, varies with the average monomer:solvent ratio in the feed. According to Equation (9), the points for $x = 0$ in Fig. 1 should lie on a straight line of unit slope, but it is obvious that less than the expected carbon tetrachloride enters the product from high carbon tetrachloride feeds. Since the very short radicals clearly have relatively less tendency to transfer than the longer ones, the persistence of this effect with increasing chain length was determined by plotting points for $x = 1$, 2, and 3 in Fig. 1. For $x = 2$, points for products averaging 6–80 styrene units fall very close to the straight line which has been drawn with unit slope. Larger or smaller values of x give marked deviations in opposite directions from this theoretical slope. These results show that, to an excellent approximation, the ratio of the rate constants for chain transfer and chain growth, *i. e.*, the transfer constant, C, is very small when $n = 1$ (C_1) and $n = 2$ (C_2), but since C_1 and C_2 are not zero, C_3 must also be at least somewhat smaller than for longer radicals. Radicals where $n \geq 4$ apparently have a substantially constant C value, the position of the straight line corresponding to $C = 0.0115$ (Equation 9, $x = 2$), in good agreement with the value of 0.0125 for very long radicals, calculated for 76° from data at 60° and 100°.[4] The approximation, that $C_1 = C_2 = 0$, which holds very well for radicals averaging six or more units, fails as the chains become shorter.

There is some uncertainty regarding the lowest monomer:solvent ratios. In these runs the molar proportion of catalyst used approaches 9% of the solvent reacting. Since every catalyst residue in the product excludes one solvent residue, the chlorine contents of the products are thereby reduced. Assuming that each molecule of catalyst used in the feed excludes one solvent residue from the product, corrected values of $\Delta M/\Delta S$ have also been calculated in Table II and plotted in Fig. 1. The corrected and uncorrected values of $\Delta M/\Delta S$, representing probable limits, are joined by a line at low solvent:monomer ratios. The correction vanishes at higher ratios.

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(9) This procedure gave 41% yield of cinnamic acid from pure 1-phenyl-1-bromo-3,3,3-trichloropropane.[3b] In these experiments, precautions were taken to recover acid from the ethyl cinnamate formed in the alcoholic silver nitrate reaction.

(10) Henle, *Ann.*, **348**, 16 (1906).

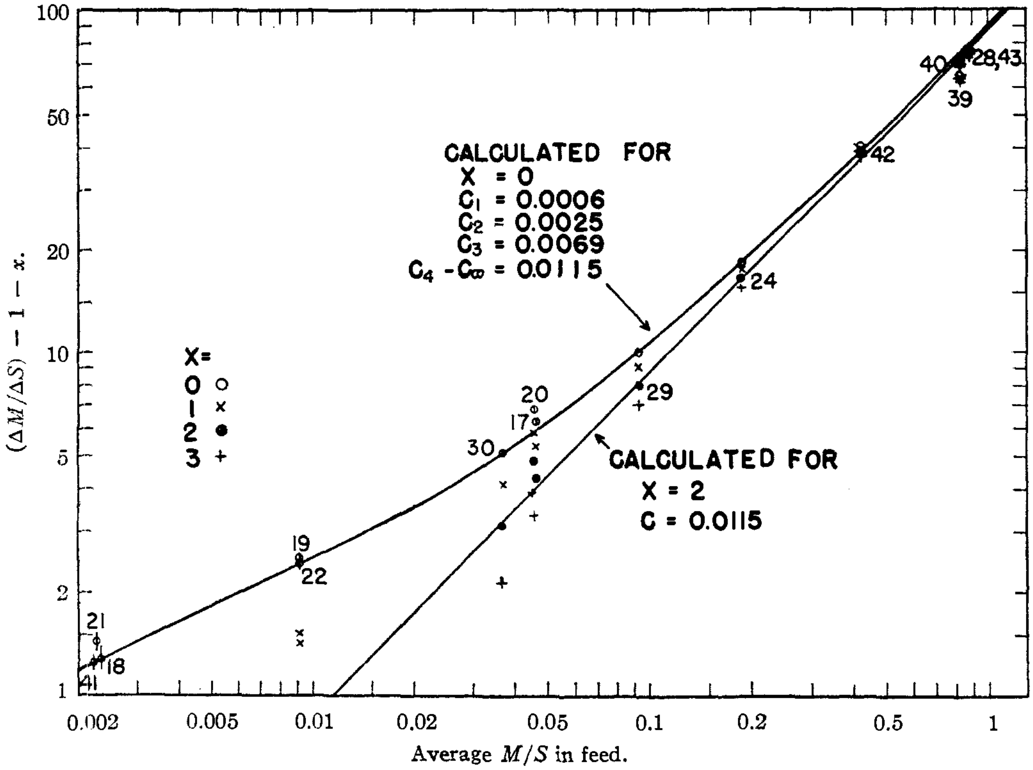

Fig. 1.—Plot of $\log \left(\frac{\Delta M}{\Delta S} - 1 - x\right) = \log M/S - \log C$.

Calculation of C_1.—The calculation of C_1 is based on the fractional distillation, at 5 mm. pressure, of products from Expts. 19, 22 and a third similar experiment and from Expt. 41, assuming that the chlorine content of the 100–150° fractions is due entirely to 1:1 adduct.

In the first case, 12.73 g. of reaction product containing 26.53% chlorine yielded 0.65 g. of a 100–150° fraction containing 35.9% chlorine, and not more than 1.645 millimoles (65%) of the 1:1 product. Since the material taken for distillation contained chlorine corresponding to 23.8 millimoles of carbon tetrachloride, by Equation (10), $C_1 = 0.00067$. In Expt. 41, 2.67 g. of product taken for distillation yielded 0.32 g. of disillate at 100–150° (43.0% Cl) and 1.76 g. at 150–210° (34.0% Cl). The 100–150° fraction cannot contain more than 0.971 millimole of 1:1 product, while the material taken for distillation contained 6.65 millimoles of carbon tetrachloride residues; $C_1 = 0.00038$. The size of the fractions makes the second result more subject to error, and the value 0.0006 has been chosen for purposes of subsequent calculation. While this value of C_1 gives excellent results in calculations of styrene:carbon tetrachloride ratios (actually, chlorine analyses) in products, the hydrolysis described in the experimental part suggests that both the quantities of 1-phenyl-1,3,3,3-tetrachloropropane and the values of C_1 calculated above are probably *maximum possible* values, the actual quantities being probably much smaller.

Calculation of C_2 and C_3.—Taking $C_1 = 0.0006$ and $C(\text{for } n \geq 4) = 0.0115$, C_2 and C_3 were determined by use of Equation (20) and the mean of the corrected and uncorrected values of $\Delta M/\Delta S$ in Table II. Graphical solution showed that Expts. 18, 22, 30 and 41 gave a remarkably consistent result; $C_2 = 0.0025$; $C_3 = 0.0069$ while an error in chlorine analysis of less than 0.1% in Expt. 29 could account for absence of perfect agreement for this experiment.

As shown by the upper curve in Fig. 1, the above values for C_1, C_2, C_3 and $C_{4-\infty}$ fit the experimental data perfectly. However, to the extent that the assumed value of C_4 is less than C_∞, the calculated value of C_3 is too low. The rather large difference between C_3 and $C_{4-\infty}$ suggests that C_3 may easily be as large as 0.008 and C_4 as small as 0.010.

Changes in Rate Constants with Radical Length.—The previous section considered the change in the ratio of the rate constants for chain transfer (k_4) and chain growth (k_3) with chain length. This section will consider changes in the ratio of the constants for chain growth and termination. It must also consider the transition from uncatalyzed to catalyzed reactions. While the uncatalyzed reaction is convenient to follow at styrene concentrations above 1 molar, it is too slow at lower concentrations. On the other hand, with the restrictions that all the catalyst but only 10–20% of the styrene must react, catalyzed experiments cannot be extended to high styrene concentrations. The over-all rate constants in the uncatalyzed runs in Table II show no effect of chain length on rate constant. These rate constants indicate that the effect of added catalyst is small in Expt. 24 but dominant in the other catalyst experiments.

Equations (16) and (17) assume that all chains end by interaction of two styrene-type ($M\cdot$) radicals. Evaluation of the quantities $(-\Delta M + \Delta S)/M[\text{Cat.}]_0^{1/2}$ and $(-\Delta S/S[\text{Cat.}]_0^{1/2})$ in catalyzed reactions (Table II) shows how the quantities $2k_3(F/k_1k_6)^{1/2}$ (Equation 16) and $2k_4(F/k_1k_6)^{1/2}$ (Equation 17) vary with the average lengths of the radicals involved. The trends are smaller than the first calculations indicate: Taking the over-all rate constant in the uncatalyzed runs as 0.00073, Expts. 24, 29 and 17, *e. g.*, are calculated to have given 9.7, 5.5, and 1.6% reaction of styrene had no catalyst been present, as compared with the observed 12.0, 14.9 and 12.3% in the presence of catalyst. However, if the calculated reactions per unit catalyst are reduced accordingly, as shown in Table II, the corrected values are too low since the combined catalyzed and uncatalyzed rates will be less than additive. The contribution of the catalyst will therefore lie in between the corrected and uncorrected values, the difference between these decreasing as the styrene concentration decreases.

Table II indicates no significant trend in the rate constant for the uncatalyzed reaction, $k_3/(k_{\text{initiation}}k_6)^{1/2}$, or in $2k_3(F/k_1k_6)^{1/2}$ as the average radical length decreases from 75 to 2, except for that due to superposition of the catalyzed and uncatalyzed reactions. Any significant changes in the rate constants for chain initiation as the medium becomes richer in carbon tetrachloride seem to be excluded since lengths of polymer radicals are not involved and since Nozaki and Bartlett[1] found that benzoyl peroxide decomposed only 40% faster in pure styrene than in pure carbon tetrachloride. Thus, the data show that both the rates of growth and interaction of the styrene-type radicals are substantially independent of chain length, or else, less probably, any change in the former (first order with respect to radicals) is balanced by an appropriate change in the latter (second order with respect to radicals and of decidedly lower activation energy) over all the radical concentrations and chain lengths studied.

On the other hand, the decrease in $2k_4(F/k_1k_6)^{1/2}$ as the average radical length decreases from twenty units to two closely parallels the decrease in average transfer constant over the same range (from 0.0102 to 0.0016 by Equation 8). The low transfer constants for short radicals therefore seem to be due mostly, if not entirely, to decreased tendencies for chain transfer rather than to increased tendencies of the radicals to grow.

If it is assumed that *all* chains terminate by reaction of two $Cl_3C\cdot$ radicals (Reaction 6a) and that $k_6 = 0$, then $2k_5(F/k_1/k_{6a})^{1/2}$ can be evaluated from $\Delta S/M[\text{Cat.}]_0^{1/2}$. Table II shows that this quantity *increases* as the radicals become shorter, but since k_5 and k_{6a} are independent of chain length and F and k_1 undergo no large change, it can only be concluded that this mechanism does not apply, that chains end largely by interaction of styrene-type radicals, as assumed for the other two equations tested. This conclusion is supported by failure to observe any hexachloroethane in any product, and by positive evidence for the formation of 1,1,1-trichloropropene, 1,1,1-trichloropropane and 1,1,1,6,6,6-hexachloro-3,4-diphenylhexane. These products show that interaction of 1-phenyl-3,3,3-trichloropropyl radicals results in both combination and disproportionation.

Acknowledgment.—Dr. H. C. Tingey of this Laboratory was the first to point out relation(10). Dr. J. R. Little carried out similar work with other monomers concurrently in this Laboratory with mutual benefit to both researches.

Summary

The rate and products of reaction of styrene with carbon tetrachloride at 76° to give mixtures of the type, $Cl_3C-(CH_2-CHC_6H_5)_n-Cl$, have been investigated. Fractions containing as much as 43% chlorine have been obtained.

The ratios of the rate constants for chain transfer and chain growth (transfer constants) for radicals containing one, two and three styrene units are 0.0006 (or less), 0.0025, and 0.007; for longer units the ratio is constant at 0.0115. Rate studies show that the trend in these ratios and the great difficulty in obtaining the lowest molecular weight products are probably due largely to changes in the rate constant for chain transfer, not in the rate constant for chain growth.

These results, together with previous work from this laboratory,[4] show that the rates of reaction of $Cl_3C-(CH_2-CHC_6H_5)_n\cdot$ radicals in addition to styrene, in interaction with each other, and in chain transfer with carbon tetrachloride (except when $n \leq 3$) are substantially independent of n over the ranges $n = 1$ to $n = 10000$, or else that any change in radical growth is compensated by a change in radical interaction.

Identification of low molecular weight products indicates that 1-phenyl-3,3,3-trichloropropyl radicals react with each other by both combination and disproportionation.

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