The greater reactivity of methacrylonitrile over methyl methacrylate in this system supports the previously proposed mechanism of anionic chain growth for polymerizations catalyzed by sodium in liquid ammonia.

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The Oxidation of Styrene

BY HAROLD BOARDMAN[1] AND P. W. SELWOOD

The mechanism of oxygen inhibition in vinyl polymerization has received considerable attention. Thus Barnes[2] showed that the induction period in photopolymerization is accompanied by substantial peroxide formation. The rate of oxygen consumption in styrene polymerization has been studied by Kolthoff and his associates,[3,4] and Medvedev and Zeitlin[5] have examined the ratio of oxidized products (benzaldehyde and formaldehyde) to polymerized products.

Goldfinger and Lauterbach[6] studied the initial rate of thermal polymerization in the presence and absence of oxygen. Samples saturated with air showed an initial higher rate of polymerization, lasting as long as twenty-eight hours, the rate then falling back to normal. An induction period was not observed in the runs in which styrene was saturated with oxygen, although it is questionable if an induction period would be evident, because, as shown in the present investigation, all the oxygen dissolved in the styrene would be consumed within thirty minutes under the experimental conditions. The over-all activation energy was found to be 16 kcal. mol.$^{-1}$.

The rate of oxygen consumption in reacting systems lends itself to measurements of magnetic susceptibility. In this way the disappearance of

Fig. 1.—Apparatus for magnetic susceptibility measurements.

molecular oxygen may be followed *in situ*, without the necessity for removal and analysis of samples. The method has the added advantage of being extremely sensitive.

During the course of the work to be described two publications appeared on the use of magnetic methods for the study of polymerizing systems. Bedwell[7] used magnetic susceptibilities, measured externally, to follow the increase of molecular weight during polymerization of methyl methacrylate. Tanaevsky[8] studied the photopolymerization, in vacuum and with oxygen inhibition, of vinyl acetate.

Some earlier uses of magnetic methods in polymerization studies gave results quite difficult of interpretation.[9-11]

Experimental Part

Preparation of Materials.—Styrene used in this work was Eastman Kodak Company white label material distilled under reduced pressure in a stream of nitrogen before use.

Benzaldehyde was also Eastman material similarly distilled.

Acetic anhydride was J. T. Baker C. P. material similarly distilled.

Sodium iodide was U. S. P. grade, recrystallized from water and dried.

Magnetic Susceptibility Measurements.—The design of the apparatus is shown in Fig. 1. A brass sample tube holder was suspended by fine copper wires about 2 meters in length. Each wire was attached at the top to a screw, for vertical adjustment; and the screw was fixed to a microscope stage, for horizontal adjustments. The whole assembly was held in place by wall brackets.

Displacement of the sample tube was measured by a filar micrometer microscope, focussed on cross hairs fixed on a cover slip attached to the brass holder.

The field was supplied by a permanent Alnico magnet,[12] having a 1-inch pole gap, 2-inch pole faces, and a field strength of 8000 gauss.

The sample tube was Pyrex glass, 12 cm. long and 1 cm. external diameter. No advantage was to be gained by using the familiar double tube in this work. In fact, any increase in weight of the sample tube may be shown to decrease the over-all sensitivity of the apparatus.

The force, f, acting on a sample of cross-section A, which extends from field H to negligible field, is given by $f = 1/2AH^2(\kappa - \kappa')$ where κ is the susceptibility per unit volume of the sample, and κ' is the susceptibility of the sur-
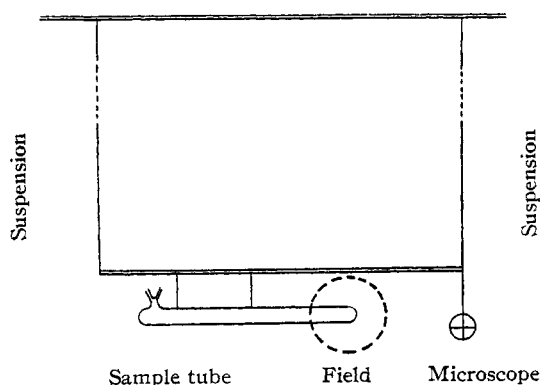
(1) Present address: Hercules Powder Company, Wilmington, Delaware.

(2) Barnes, THIS JOURNAL, **67**, 217 (1945).

(3) Kolthoff and Dale, *ibid.*, **69**, 441 (1947).

(4) Bovey and Kolthoff, *ibid.*, **69**, 2143 (1947).

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

(6) Goldfinger and Lauterbach, *J. Polymer Sci.*, **3**, 145 (1948).

(7) Bedwell, *J. Chem. Soc.*, 1350 (1947).

(8) Tanaevsky, *Compt. rend.*, **225**, 1069 (1947).

(9) Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936).

(10) Farquharson and Ady, *Nature*, **143**, 1067 (1939).

(11) Bhatnagar, Kapur and Kaur, *J. Indian Chem. Soc.*, **17**, 177 (1940).

(12) The magnet was made for this work by the Indiana Steel Products Company, Chicago, Illinois.

rounding atmosphere. From the geometry of the apparatus it is readily shown[13] that a sample undergoing a change of susceptibility, $\Delta\kappa$, will suffer a proportional displacement, D, or that

$$D = c\,\Delta\kappa = c\rho\,\Delta\chi \qquad (1)$$

where c is a constant, ρ the density, and $\Delta\chi$ the change in susceptibility per unit mass. It is assumed that the density is constant (so far as influence on D is concerned) and this may readily be shown for all the samples investigated in this work.

Determination of the constant c was made by four different methods, three of which were in agreement. From the geometry of the apparatus $c = H^2AL/2Mg$ where L is the length of the suspension wires, M is the mass of sample tube and contents, and g is the gravitational constant. By inserting the proper values c is found to be 1×10^5.

A more accurate calibration was made by using the reduction of dichromate to chromic ions. In this reaction the velocity of reduction may be controlled by altering the acidity, and the magnetic change which occurs is almost solely due to the changing concentration of chromic ion.

A 50-cc. sample of 4% potassium dichromate solution was mixed with 40 cc. of an 18% glucose solution, and 10 cc. of approximately 5 N sulfuric acid. The reaction mixture was immersed in a constant temperature bath. A sample of the reaction mixture was now withdrawn and placed in the magnetic sample tube, the temperature of which had previously been adjusted to be the same as that of the bath. A sample was also withdrawn from the bath for dichromate analysis by the standard thiosulfate method. At frequent time intervals magnetic displacements and dichromate concentrations were observed, it being assumed that the reaction velocity in the bath would be the same as in the magnetic balance, because both were at the same temperature.

Data for this "dichromate" calibration are shown in Fig. 2. We make the assumption that all magnetic changes are negligible compared with that produced by the changing chromic ion concentration. Hence, it may readily be shown that the apparatus constant, c, is given by

$$c = \frac{\partial D}{\partial S} \times \frac{1}{4.14 \times 10^{-3}} \qquad (2)$$

where S is the thiosulfate titration. The calibration constant is shown in Table III.

A third calibration was made by using the fact that the susceptibility of nickel chloride solution changes with temperature. According to Nettleton and Sugden[14] the susceptibility, χ, of such a solution is given by

$$10^6\chi = (10030\chi/T) - 0.720(1 - \chi) \qquad (3)$$

where χ is the weight fraction of nickel chloride present. It then follows that

$$c = DT_1T_2/10^{-2}\rho\chi\,\Delta T \qquad (4)$$

where T_1T_2 are two temperatures at which measurements were made, and ΔT is the temperature interval. The data are shown in Table II, and the apparatus constant so obtained is shown in Table III.

The "blank" displacement was that observed when the sample tube was filled with water and the temperature raised from T_1 to T_2. It is, in part

(13) H. Boardman, Thesis, Northwestern University, Evanston, Illinois, 1948.

(14) Nettleton and Sugden, *Proc. Roy. Soc. (London)*, **A173**, 313 (1930).
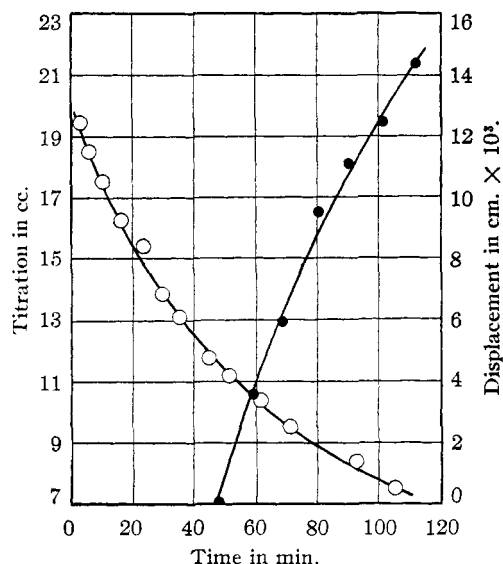

Fig. 2.—"Dichromate" calibration curves, titration O, magnetic displacement ●.

at least, due to traces of paramagnetic substances present in the glass, and in part to changing surface tension effects on the suspension wires.

TABLE I

"NICKEL CHLORIDE" CALIBRATION

Concentration of solution	22.3% by weight $NiCl_2$
Density	1.243 g./cc.
T_2	306.6 °K.
T_1	303.9 °K.
Displacement	4.5×10^{-3} cm.
Blank displacement	-2.4×10^{-3} cm.
Corrected displacement	6.9×10^{-3} cm.

In the course of studying oxygen consumption in styrene it soon became evident that if the mass susceptibility of gaseous oxygen, and the calibration previously determined, were used to calculate rates of reaction, then the rate of oxygen consumption appeared to be abnormally high. Consequently, it was decided to determine the apparatus constant by a direct calibration with oxygen. The procedure will be described in detail because it illustrates the method used in determining the rate of oxygen consumption.

The over-all reaction of oxygen with styrene may be represented as

$$C_6H_5CH{=}CH_2 + O_2 \longrightarrow C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}{-}H + CH_2O$$
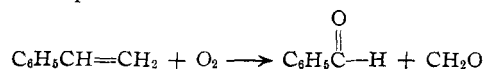
As the reaction proceeds, the change in magnetic susceptibility is given by the Wiedemann law

$$\Delta\chi_s = (\chi\Delta W)_{O_2} + (\chi\Delta W)_{C_8H_8} - (\chi\Delta W)_{C_7H_6O} - (\chi\Delta W)_{CH_2O} \qquad (5)$$

where χ and W are the mass susceptibilities and weight fractions, respectively, of the several components. But the susceptibilities of all compo-

nents are so small in comparison with that of oxygen that the equation reduces to

$$\Delta x_s = (x \Delta W)_{O_2} \tag{6}$$

If it is assumed that the susceptibility of oxygen dissolved in styrene is the same as that of gaseous oxygen, namely, $0.993/32T$, then since $\Delta W_{O_2} = \Delta[O_2] \times 32/1000p$, equation 6 reduces to

$$\Delta x_s = 0.993 \, \Delta[O_2]/1000 \tag{7}$$

and substituting equation 7 into equation 2

$$\Delta[O_2] = 10^3 DT/0.993c \tag{8}$$

Oxygen calibration was performed with the apparatus shown in Fig. 3, as follows: The magnetic sample tube was filled with styrene (preparation below) and then frozen with Dry Ice, after which the sample tube was sealed to the apparatus shown in Fig. 3. The apparatus was evacuated, then
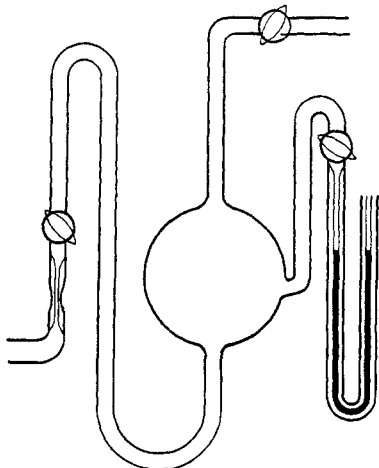

Fig. 3.—"Oxygen" calibration apparatus.

any molecular oxygen dissolved in the styrene was destroyed by heating the sample tube for two hours at 50°. The styrene was frozen again, oxygen was admitted to the apparatus, and, by proper manipulation of the stopcocks, a known volume of oxygen was admitted to the styrene. This volume was measured by observing the change in the mercury manometer. Finally, the sample tube was removed by sealing off the connecting tube. The sample tube was then placed in the magnetic balance where deflections were observed until no further magnetic change occurred.

Typical calibration data obtained in this way are shown in Table II.

TABLE II

OXYGEN CALIBRATION OF MAGNETIC BALANCE

Temperature of reservoir, °C.	21.8
Change of pressure, ΔP	15.9 mm.
Correction for capillary	0.9 mm.
Corrected ΔP	15.0 mm.
Volume of reservoir	79.1 cc.
Volume of styrene	11.3 cc.
Temperature of displacement run	~48.0°
Total displacement	7.3×10^{-5} cm.

From the above data it is seen that the initial concentration of oxygen $[O_2]$ in the styrene is

$$[O_2] = \frac{79.1 \times 15.0 \times 293}{22.4 \times 760 \times 295 \times 11.3} = 5.7 \times 10^{-3} \text{ moles per liter}$$

and the apparatus constant

$$c = \frac{10^3 \times 7.3 \times 10^{-5} \times 321}{0.993 \times 5.7 \times 10^{-3}} = 4.1 \times 10^5$$

Concordant results were obtained on a second run.

The calibration data are summarized in Table III.

TABLE III

CALIBRATION CONSTANTS

	$k \times 10^{-5}$
Geometrical calibration	1
Dichromate	0.99
Nickel chloride	0.86
Oxygen	4.1

Some very intensive investigations failed to yield a reason for the deviation, from what appears to be the true calibration, in the case of oxygen. For our present purposes the rate constants are important, and not the total magnitudes of oxygen consumption. For that reason the matter was not pursued further for the present, and the oxygen calibration was used, as likely to yield more accurate results for the particular reaction under study.

Peroxide and Benzaldehyde Determinations.—The method used for peroxide determination was measurement of the optical density of the solution of iodine released by action of the peroxide on an acetic anhydride solution of sodium iodide. Freshly distilled styrene was placed in a three-necked flask, equipped with a liquid seal stirrer, an oxygen inlet tube extending below the surface of the styrene, and an outlet tube, slightly constricted to maintain a positive oxygen pressure within the flask. The flask was kept at $48.5 \pm 0.2°$. During a run, oxygen was bubbled through the styrene and vigorous stirring was maintained. At periodic intervals 2-cc. samples were withdrawn and placed in glass-stoppered weighing bottles. The styrene was immediately frozen by placing the weighing bottle on a block of Dry Ice in an air-tight box through which a stream of carbon dioxide was passing.

Freshly distilled acetic anhydride and recrystallized sodium iodide had previously been placed in containers in the box.

When the run was completed, the sodium iodide was dissolved in the acetic anhydride (80 g. l.$^{-1}$) and 11.4 cc. of this reagent was added to each sample of styrene from an automatic pipet. The samples were allowed to stand for twenty minutes and, at the end of this time, quartz absorption cells were filled with the samples. The cells were capped, removed from the box and placed in a Beckman spectrophotometer to determine the optical density of the liberated iodine solution at 4000 Å., using reagent as the reference solution.

Figure 4 shows the calibration curve for the determination of peroxide concentration.

Benzaldehyde was estimated by Medvedev and Zeitlin by shaking a sample of styrene with dilute sodium bisulfite and titrating the excess bisulfite with standard iodine solution. Such a procedure was not applicable in the present work because of the small quantity of benzaldehyde formed during the initial phase of the reaction. A spectrophotometric method was therefore used. The procedure was similar to that for peroxide determination. Samples of partially oxygenated styrene were removed
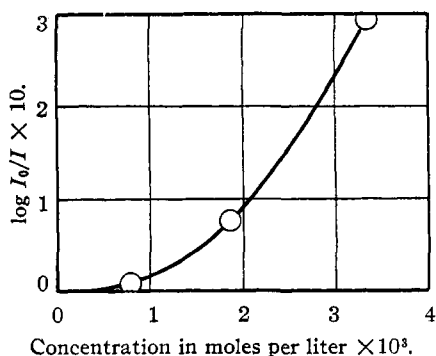
Fig. 4.—Peroxide calibration.

from the reaction flask at periodic intervals and were frozen until ready for measurement of optical density at 3330 Å. A calibration curve was obtained by measuring the optical densities of solutions of benzaldehyde in styrene at 3330 Å. Beer's law is obeyed over the whole range of concentration, and the molar extinction coefficient is 33.8. It is to be noted that had the styrene polymerized to any appreciable extent erroneous results would have been obtained. But as the molar extinction coefficient of unpolymerized styrene at 3330 Å. is only 5.8×10^{-3}, and as little or no polymerization took place under the experimental condition, no difficulty was experienced.

Results

Rate of Oxygen Consumption.—Data for the rate of oxygen consumption in pure styrene at 48.5° are shown in Fig. 5. Run no. 3 has been shifted thirty minutes to the right for convenience. The curved portions of runs nos. 1 and 2 were found to be due to diffusion of oxygen into the sample through the inlet to the sample tube. This effect was eliminated in run no. 3 by plugging the inlet with a ground-in capillary.
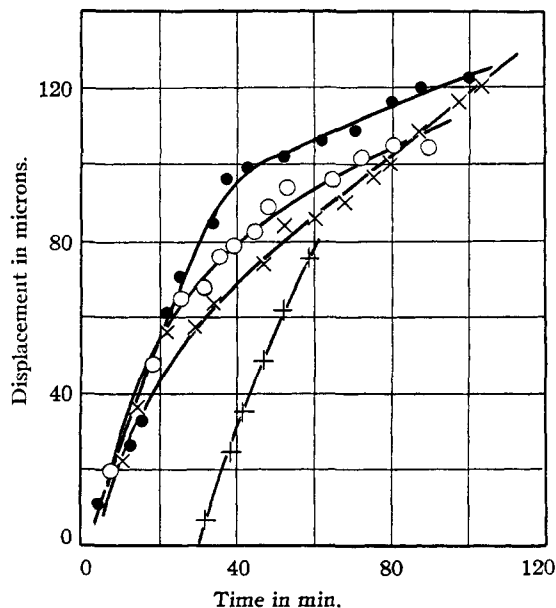

Fig. 5.—Oxygen consumption: data for four different runs are shown.

It is at once evident that the rate of oxygen consumption is zero order, which suggests that the rate is dependent on some controlling step, which is presumably the formation of activated monomer molecules with which the oxygen reacts. The rate of oxygen consumption is given by

$$\frac{-d[O_2]}{dt} = \frac{10^3 T}{0.99 \times 4.1 \times 10^5} \frac{\partial D}{\partial t} \qquad (9)$$

The calculated rate is given in Table IV.

Phenolic compounds such as hydroquinone and t-butylcatechol are not direct inhibitors of polymerization.[15] This type of compound exerts its stabilizing effect by preventing the formation of peroxides which can act as catalysts in initiating polymerization. The action of oxygen on active vinyl monomers undoubtedly involves the formation of an active peroxide free radical.[16] The stabilizing action of antioxidants on such systems consists in reacting with peroxides or peroxide free radicals.

If an antioxidant reacts with the peroxide free radicals as soon as they are formed, it should decrease the rate of oxygen consumption by stopping the chain reaction of oxygen. But the antioxidant should not completely stop the oxygen consumption because the oxygen is still capable of reacting with activated monomer molecules. Assuming that the antioxidant reacts with all the peroxide free radicals formed, then the rate of oxygen consumption in styrene in which such an antioxidant has been dissolved should give the rate of initiation of activated monomer molecules, and also the kinetic chain length for the reaction of oxygen with styrene.

The rates of oxygen consumption in the presence of t-butylcatechol and of hydroquinone are shown in Fig. 6.
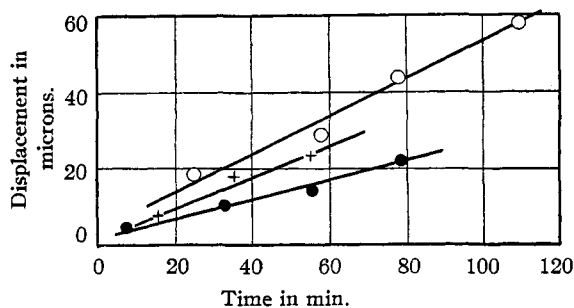
Fig. 6.—Oxygen consumption in the presence of antioxidant, t-butyl catechol at 57.7°, O; hydroquinone at 56.9°, +; t-butylcatechol at 48.5°, X.

The initiation process will be discussed later. For the present it is assumed that activated monomer molecules are produced by a bimolecular process such that

$$-\partial[O_2]/\partial t = k_1 M^2 \qquad (10)$$

(15) Walling and Briggs, THIS JOURNAL, **68**, 1141 (1946).
(16) Waters, "The Chemistry of Free Radicals," Oxford University Press, Oxford, 1946, p. 197.

where k_1 is the rate constant for initiation and M is the concentration of monomer molecules. The density of styrene in this temperature range is 0.89 g./cc., hence $M = 8.6$ moles/l. The constants k_1 calculated from equations 9 and 10, and the data of Fig. 6, are given in Table IV. A plot

TABLE IV

RATES OF OXYGEN CONSUMPTION AND RELATED DATA

No.	Temp., °K.	Condition	$-\partial O_2/\partial t$ (moles l.$^{-1}$ min.$^{-1}$)	k_1, (moles^{-1} l.$^{-1}$ m.$^{-1}$)
1	321.5	Styrene satd. with air	2.1×10^{-4}	
2	321.5	1 plus t-butylcatechol	2.4×10^{-5}	3.4×10^{-7}
3	329.9	1 plus hydroquinone	3.7×10^{-5}	5.3×10^{-7}
4	330.7	1 plus t-butylcatechol	4.1×10^{-5}	5.8×10^{-7}

$E_1 = 12$ kcal./mole; kinetic chain length $= 8.8$.

of $\log k_1$ against $1/T$ is given in Fig. 7 from which the activation energy for initiation, E_1, may be calculated. The kinetic chain length for oxygen consumption at a given temperature is given by the ratio of the rate of oxygen consumption in the absence and the presence of antioxidant, respectively. These data are also given in Table IV.
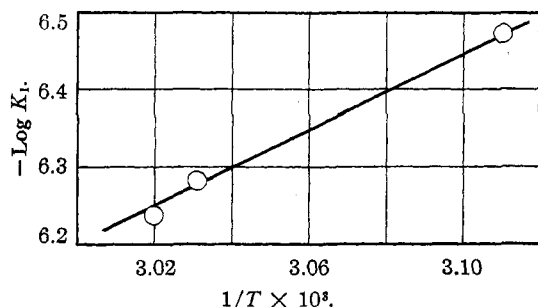

Fig. 7.—Log K_1 vs. $1/T$ from the data of Fig. 6.

Peroxide and Benzaldehyde Formation.—The data for peroxide formation are shown in Fig. 8.

The data on benzaldehyde formation at $48.5 \pm 0.2°$ are given in Fig. 9. These data are somewhat erratic but give a fair idea as to the rate of formation of benzaldehyde, which, from these data, is 0.8×10^{-4} mole l.$^{-1}$ min.$^{-1}$.

Some attempts were made to separate polymer from the reacting styrene, but the amount formed was so small that all such attempts were unsuccessful. Thus, air was passed through styrene, held at 48.5° for twenty-four hours. At the end of that time an excess of methyl alcohol was added to the styrene, and only a very small amount of polymer precipitated. It may be concluded that polymerization cannot take place in this system, at this temperature, so long as oxygen is present, and not too high a concentration of peroxides has accumulated.

Discussion of Results

Initiation.—The activation energy for the initiation step in the oxidation of styrene has been found in this work to be 12 kcal. mole^{-1}. If this is correct, then it is obvious that this step cannot involve the direct formation of free radi-
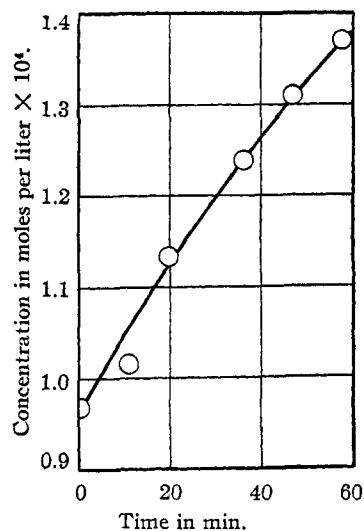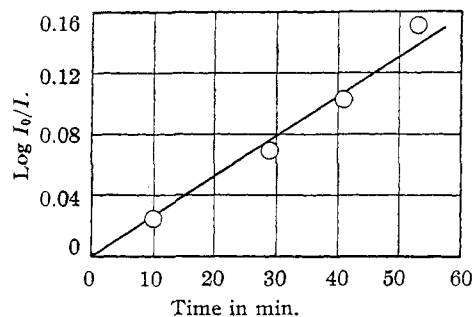

Fig. 8.—Rate of peroxide formation.

Fig. 9.—Rate of benzaldehyde formation.

cals, because such a process[17,18] involves an activation energy of approximately 30 kcal. mole^{-1}. It is suggested, therefore, that initiation in the oxidation of styrene simply requires the formation of activated styrene molecules. It is to be noted that George and Robertson[19] found that the chain carriers in the oxidation of tetralin are energy-rich molecules. The oxidation of styrene and the thermal polymerization of styrene are not necessarily initiated by the same type of molecular species, although Irany[20] objects to thermal polymerization being initiated by free radicals.

Bovey and Kolthoff[4] found that the oxidation of styrene in emulsion, when initiated by persulfate, resulted in the almost exclusive formation of a peroxide polymer. In the present work, the data on benzaldehyde formation, although admittedly approximate, show that most of the oxygen reacts with the styrene to form benzaldehyde (and formaldehyde). The rate of accumulation of peroxide is only 0.004 times the rate of oxygen consumption. The rate curve follows the kinetic expression

(17) Flory, THIS JOURNAL, 59, 241 (1937).
(18) Bamford and Dewar, Proc. Roy. Soc. (London), A192, 309 (1948).
(19) George and Robertson, ibid., 185, 309 (1946).
(20) E. P. Irany, THIS JOURNAL, 62, 2690 (1940).

$$dP/dt = K - K'P$$

that is, the simultaneous formation (from some steady-state process) and decomposition of peroxide.

It would seem that the initiation process could be represented by activated styrene reacting with oxygen to yield a peroxide readical which disproportionates to benzaldehyde and formaldehyde.[20] The energy-rich benzaldehyde, possibly together with the formaldehyde may carry on the chain reaction as suggested by Medvedev and Zeitlin.[5] The short chain length found in this work is explicable on the basis of a chain carrier with a short mean free life, which would be expected for an energy-rich molecule. It is not clear whether the peroxide that accumulates slowly is the resonance stabilized peroxide, $C_6H_5CH-CH_2$, or a further reaction product. $\overset{|}{O}-\overset{|}{O}$

Our conclusions are necessarily dependent upon the assumption that the antioxidants almost completely suppress the chain reaction. This would seem to be difficult to prove experimentally but seems likely, inasmuch as such antioxidants prevent the formation of catalysts (peroxides produced by the action of oxygen on the monomer and accumulated benzaldehyde) capable of initiating polymerization, and that this inhibition operates as long as excess antioxidant is present. On the other hand it must be admitted that the inactivation of all peroxide radicals with the antioxidants employed is not infrequently found to be a difficult thing to do.

Bolland and Ten Have[21] have studied the relative efficiencies of the inhibitory effect of phenolic compounds on the thermal oxidation of ethyl linoleate. These compounds differ in their efficiency (as measured by oxygen consumption in the presence and absence of antioxidant) according to their oxidation–reduction potential and concentration. Thus, catechol is only about 0.6 times as efficient as hydroquinone. As is evident from Fig. 7 of this work t-butylcatechol is as efficient as hydroquinone in suppressing oxygen consumption (the styrene was saturated with antioxidant in both cases). This equality in efficiency is explicable on the basis that nearly all the oxidation chains are stopped.

The results on peroxide formation and benzaldehyde formation support the usual concepts of an autoxidation process with a peroxide occurring as an intermediate compound in the process.

It is a pleasure to acknowledge the support of the United States Rubber Company in connection with this work.

Summary

A magnetic susceptibility method has been used to measure the rate of oxygen consumption during the initial stages of styrene polymerization. Measurements were made with and without the addition of antioxidants. The rates of formation of peroxide and of benzaldehyde in this system have also been determined.

From these data calculations were made of the rate constant for initiation and the kinetic chain length for the reaction of oxygen with styrene, as well as the activation energy for initiation.

Evanston, Illinois   Received June 9, 1949

(21) J. L. Bolland and P. Ten Have, *Discussions of the Faraday Soc.*, **252** (1947).

The Dipole Moments of Some Derivatives of Trichlorosilane

By H. O. Spauschus, A. P. Mills,[1] J. M. Scott and C. A. MacKenzie

The dipole moments have been determined for a series of ethyl and ethoxy derivatives of trichlorosilane. The compounds investigated were trichlorosilane, ethyldichlorosilane, diethylchlorosilane and triethoxysilane; all measurements were made in benzene solution.

Previous investigators have measured the dipole moments of tetraethoxysilane,[2] some chlorosilanes,[3] silicobromoform,[4] ethyl and phenyl derivatives of tetrachlorosilane and tetrafluorosilane,[5] and compounds containing triethylsilyl and triphenylsilyl radicals.[6]

Experimental

Dielectric Constant.—All measurements were made using a heterodyne beat apparatus similar to that of Hudson and Hobbs[7] with several modifications to increase the stability. The experimental cell and precision condenser (General Radio Company, type 722-D) were kept in a constant temperature air bath at $25.00 \pm 0.05°$. The variable oscillator was also kept at a constant temperature to minimize possible frequency drift. Radio broadcasts were used as sources of constant frequency. All capacity measurements were made at three different frequencies. The all glass experimental cell consisted of two concentric cylinders coated with platinum, and had a volume of

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(2) W. J. Svirbely and J. J. Lander, This Journal, **70**, 4121 (1948).

(3) L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(4) G. L. Lewis and C. P. Smyth, This Journal, **61**, 3063 (1939).

(5) P. A. McCusker, R. M. Witucki and C. Curran, Abs. of Papers, 112th meeting, Am. Chem. Soc., 0–6 (1947).

(6) L. Malatesta and R. Pizzotti, *Gazz. chim. ital.*, **72**, 491 (1942); **73**, 143 (1943).

(7) B. E. Hudson and M. E. Hobbs, *Rev. Sci. Instruments*, **13**, 140 (1942).