Summary

1. The sulfonation of methallyl chloride by dioxane sulfotrioxide gives a complex mixture of products. About 40% of the sulfur trioxide reacts by addition to the double bond to give a cyclic anhydride of the carbyl sulfate type. The remainder reacts by substitution to give three isomeric chloroisobutylenesulfonic acids.

2. In contrast to isobutylene, methallyl chloride is neither polymerized nor disulfonated by the dioxane sulfotrioxide.

3. It has been found that the olefinic linkage in a variety of unsaturated sulfonic acids is mobile in the presence of alkali.

4. The ozonization of 2-methylpropene-1,3-disulfonyl chloride confirmed the structure previously assigned to this compound. An attempt to prepare sodium 2-methylenepropane-1,3-disulfonate was unsuccessful, the double bond shifting into the chain.

5. The sulfonation of methallyl chloride by a solution of sulfur trioxide in ethylene chloride yields chiefly the carbyl sulfate type of compound. The hydrolysis reactions of this were studied in some detail.

6. The sulfonation of methallyl chloride with sodium chlorosulfonate gives a mixture of unsaturated sulfonic acids.

7. Numerous compounds have been prepared from the chloroisobutylenesulfonic acids during attempts to determine their structures.

Evanston, Ill. Received December 10, 1942

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Polymerization of Styrene in the Presence of 3,4,5-Tribromobenzoyl Peroxide

By Charles C. Price and Bryce E. Tate

Samples of polystyrene, prepared by heating solutions of styrene and 3,4,5-tribromobenzoyl peroxide in benzene and purified by repeated reprecipitation from ether or dioxane by pouring into alcohol have been found to contain as much as 15% bromine. On the basis of the average molecular weights of the samples, as measured repeatedly by both the cryoscopic and viscometric methods, the bromine content of each sample corresponded to approximately one tribromophenyl radical per polymer molecule.

Since the polymers were of relatively low molecular weight, in the range of one to three thousand, fairly reliable estimates of the molecular weight were obtained by cryoscopic determinations, using *p*-nitrotoluene and, in a few instances, benzophenone for the solvent. These cryoscopic values for the molecular weight were found to agree satisfactorily with the viscometric measurements, using the revised[1] value for the constant of the Staudinger equation relating viscosity of polymer solutions to the molecular weight of the polymer.[2]

Using the Kemp and Peters equation, the values for the viscometric molecular weights of various samples of polystyrene prepared in the presence of anisoyl, *p*-bromobenzoyl and chloroacetyl peroxides would be just half those we previously recorded[3] and the average number of end groups per polymer molecule calculated on the basis of the recalculated viscometric molecular weights, 0.93 ± 0.37, now agrees satisfactorily with the average calculated on the basis of the cryoscopic molecular weights, 1.07 ± 0.41 and both these values are in good agreement with the more accurate results reported herein for tri-bromobenzoyl peroxide.

The accumulation of data thus points to the presence of one fragment from the catalyst per polymer molecule. If active growing polymer chains, initiated by a free radical derived from decomposition of the catalyst, were to be stabilized by disproportionation of hydrogen with some other radical in the solution, the polymer molecules so formed would each contain one fragment from the catalyst.

$$\text{A.}\quad \left.\begin{array}{r} (C_6H_5CO_2)_2 \rightleftarrows 2C_6H_5CO_2^{\cdot} \\ \downarrow\quad \\ CO_2 + C_6H_5^{\cdot} \end{array}\right\} R^{\cdot}$$

$$\text{B.}\quad R^{\cdot} + CH_2{=}CHX \longrightarrow RCH_2CHX^{\cdot} \longrightarrow\longrightarrow R(CH_2CHX)_nCH_2CHX.$$

$$\text{C.}\quad R(CH_2CHX)_nCH_2CHX^{\cdot} + R(CH_2CHX)_mCH_2CHX^{\cdot} \longrightarrow R(CH_2CHX)_nCH{=}CHX + R(CH_2CHX)_mCH_2CH_2X$$

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[1] Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

[2] Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

[3] Price, Kell and Krebs, This Journal, **64**, 1103 (1942).

$$R(CH_2CHX)_nCH_2CHX\cdot + R\cdot \longrightarrow R(CH_2CHX)_nCH{=}CHX + RH$$
$$R(CH_2CHX)_nCH_2CHX\cdot + RCO_2\cdot \longrightarrow R(CH_2CHX)_nCH{=}CHX + RCO_2H$$

Since active free radicals, such as those from the decomposition of peroxides, will substitute in aromatic nuclei,[4] consideration has been given to the possibility that the fragments from the peroxide might have been incorporated in the polymer by reaction with a phenyl group of the styrene residues.

It seemed unlikely that such could be the case because polymethyl methacrylate, with no phenyl group, was found to contain fragments from the catalyst in the same proportion as polystyrene.[3] The possibility was tested experimentally by treating a solution of polystyrene with 3,4,5-tribromobenzoyl peroxide under the conditions used for polymerization. The polymer so obtained was found to contain less than 1% bromine, corresponding to only about one tribromophenyl group for every seventeen polymer molecules. The assumption that the fragments of the catalyst are incorporated in the polymer during the polymerization process is therefore substantiated.

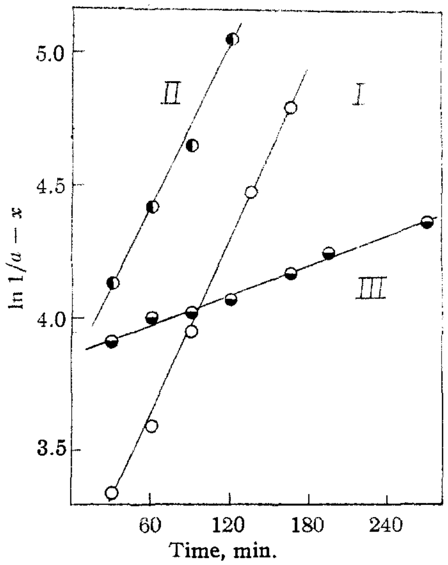
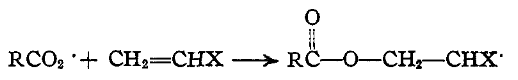


Fig. 1.—First order kinetics for decomposition of 3,4,5-tribromobenzoyl peroxide at 80°: I and II, during polymerization of styrene in benzene ($k = 0.0102$ and 0.0108); III, in benzene with polystyrene present ($k = 0.0019$).

Since styrene will polymerize slowly in the absence of a catalyst under the conditions employed, it was essential to interrupt the polymerization when the peroxide had disappeared in order to minimize the formation of polymer molecules which would have no chance to contain fragments from the catalyst. We have therefore followed the rate of disappearance of the 3,4,5-tribromobenzoyl peroxide during the course of polymerization. Samples were removed periodically and pipetted into potassium iodide in acetone; the liberated iodine was then titrated with standard sodium thiosulfate solution. The same measurement was also made during the course of the reaction of 3,4,5-tribromobenzoyl peroxide and polystyrene in benzene solution under similar conditions. In both cases, the rate of disappearance of peroxide followed first order kinetics very satisfactorily (Fig. 1). The rate constant for the disappearance of peroxide during the polymerization was, however, six times that during the thermal decomposition. Kamenskaya and Medvedev[5] have reported a similar observation; they found that benzoyl peroxide was decomposed twice as fast in the presence of vinyl acetate as it was under similar conditions in the absence of monomer and suggested the formation of an active complex between monomer and catalyst as an explanation. This is not in agreement with our interpretation of the kinetics of the benzoyl peroxide-catalyzed polymerization of *d-s*-butyl α-chloroacrylate[6] and we contemplate a more thorough investigation of the factors affecting the decomposition of acyl peroxides.

The analytical data accumulated during the investigation indicated that all the polymer samples contained varying amounts of oxygen, whether prepared by benzoyl or tribromobenzoyl peroxide catalysis in either dioxane or benzene. The source and functional nature of the oxygen has not yet been determined. In many instances, the oxygen content was considerably in excess of that required for a benzoxy rather than a phenyl group at the end of the polymer chains. The polymerizations were carried out with no particular



$$RCO_2\cdot + CH_2{=}CHX \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2{-}CHX\cdot$$

precautions to exclude air since many samples of polymer prepared under apparently similar conditions had been found to contain little or no oxygen.[3] The contamination with oxygen must have occurred during polymerization rather than puri-

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[4] See Hey and Waters, *Chem. Rev.*, **21**, 169 (1937); Fieser, Clapp and Daudt, THIS JOURNAL, **64**, 2052 (1942); Fieser and Oxford, *ibid.*, 2060.

[5] Kamenskaya and Medvedev, *Acta Physicochim., U. S. S. R.*, **13**, 565 (1940).

[6] Price and Kell, THIS JOURNAL, **63**, 2798 (1941).

fication since a solution of an oxygen-free polystyrene sample was unchanged after standing three days in the sunlight in contact with air in dioxane giving a strong positive test for peroxide with potassium iodide. The factors influencing the contamination of the polymer by oxygen are to be investigated further.

Experimental[7]

3,4,5-Tribromobenzoyl Peroxide.—The preparation of 3,4,5-tribromobenzoic acid from *p*-aminobenzoic acid by bromination followed by diazotization according to the directions of Sudborough[8] was found to be much more satisfactory than from 3,4,5-tribromotoluene either by direct oxidation or by bromination according to Asinger.[9] 3,4,5-Tribromobenzoic acid, m. p. 235–240°, was obtained in 60% over-all yield from *p*-aminobenzoic acid. Conversion of the acid to the chloride was accomplished by treatment with thionyl chloride, removal of excess thionyl chloride by evaporation under diminished pressure and recrystallization from low-boiling petroleum ether.

The recrystallized acid chloride was dissolved in benzene and the solution was added slowly with stirring to one equivalent of sodium peroxide in water at 0–5°. The 3,4,5-tribromobenzoyl peroxide was collected by filtration and recrystallized from toluene preheated to 80–85°; m. p. 183–185°; yield, 18%.

Anal. Calcd. for $C_{14}H_4O_4Br_6$: C, 23.43; H, 0.55. Found: C, 23.81, 23.89; H, 0.77, 0.87.

Polymerization with 3,4,5-Tribromobenzoyl Peroxide.—I. 3,4,5-Tribromobenzoyl peroxide (2 g.) was added to 50 cc. of a 20% solution of redistilled styrene in benzene. The mixture was boiled under reflux for six hours, the benzene was evaporated under diminished pressure and the residue was dissolved in dioxane. Addition of alcohol precipitated 1.8 g. (18%) of polystyrene. Before analysis the polymer was reprecipitated three times from dioxane by pouring into alcohol. The molecular weight was measured cryoscopically in *p*-nitrotoluene,[10] and viscometrically in tetralin.[11]

Anal Calcd. for $Br_3C_6H_2(C_6H_8)_{12}O_3$: C, 76.02; H, 6.13; Br, 14.87; O, 2.98; mol. wt., 1610. Found: C, 76.27; H, 6.15; Br,[12] 14.40, 15.05; O (by difference), 2.85; mol. wt. (cryosc.), 1710, 1880, 2390; (visc.), 1430.

The rate of disappearance of the peroxide during the polymerization was measured by withdrawing 1-cc. samples of the reaction mixture at specified intervals. These samples were added to 10 cc. of 12.8% potassium iodide in acetone and the iodine liberated by the peroxide was titrated with standard aqueous thiosulfate. The rate data obtained for this experiment are summarized in Fig. 1 (I).

II. A second polymerization in benzene was carried out in the same manner as I, except that twice as much material was used. The polystyrene was purified by several reprecipitations from dioxane by pouring into alcohol.

Anal. Calcd. for $Br_3C_6H_2(C_8H_8)_{15}O_7$: C, 76.12; H, 6.19; Br, 12.06; O, 5.63; mol. wt., 1990. Found: C, 76.02; H, 6.10; Br, 13.22,[12] 11.04 (combustion); O (by difference), 5.75, mol. wt. (cryosc.), 1160, 1240; (visc.), 1400.

The data for the rate of decomposition of the peroxide during this polymerization are summarized in Fig. 1 (II).

A third sample of polystyrene was prepared by heating 3.4 g. of 3,4,5-tribromobenzoyl peroxide in 50 cc. of a 20% solution of styrene in dioxane at 95° for eighteen hours The solution was cooled and the polymer was precipitated by pouring into alcohol. The polystyrene was purified for analysis and molecular weight determination by three reprecipitations from dioxane by pouring into alcohol.

Anal. Calcd. for $Br_3C_6H_2(C_8H_8)_{36}O_{19}$: C, 80.86; H, 6.69; Br, 5.49; O, 6.96; mol. wt., 4370. Found: C, 80.82; H, 6.72; Br, 5.51; O (by difference), 6.95, mol. wt. (cryosc. in *p*-nitrotoluene), 2520, 3020, 2620; (in benzophenone), 3000; (visc.), 3200.

In this polymerization, the reaction mixture was heated considerably longer than the time required for the complete decomposition of the catalyst. A portion of the polymer may thus have resulted from thermal polymerization and would therefore contain no fragments from the catalyst. For the molecular weight observed, the bromine analysis would indicate that only two out of three polymer molecules contained a tribromophenyl end group.

Polystyrene plus 3,4,5-Tribromobenzoyl Peroxide.—Polystyrene (10 g.) with a molecular weight of 1100 (visc.), which had been prepared in benzene solution with benzoyl peroxide as a catalyst, was dissolved in 40 cc. of benzene and heated under reflux with 1 g. of 3,4,5-tribromobenzoyl peroxide. After the usual precipitation and purification, the polymer was found to contain a small amount of bromine.

Anal. Found: C, 90.34; H, 7.70; Br, 0.87, 0.88; mol. wt., 1450 (visc.).

The rate of decomposition of the peroxide was measured during this experiment and was found to be very much slower (six-fold) than that during the polymerizations (I and II). The data are summarized in Fig. 1 (III).

Oxypolystyrene.—A sample of polystyrene was prepared by heating 150 cc. of a 20% solution of styrene in dioxane with 1.9 g. of benzoyl peroxide on a steam-bath for sixteen hours. The polymer was purified in the usual manner.

Anal. Calcd. for $C_8H_5(C_6H_8)_{31}O_3$: C, 90.91; H, 7.63; mol. wt., 3275. Found: C, 90.87; H, 7.66; mol. wt., 2800 (visc.).

In a single preliminary experiment to determine whether the oxygen might have entered the polymer chain as ether or peroxide links between monomer units, 11 g. of the above sample of oxypolystyrene was boiled under reflux with 200 cc. of glacial acetic acid and 100 cc. of concentrated hydriodic acid solution for eight hours. The mixture was diluted with water and the polymer (8.3 g., 75%) separated by extraction with benzene. The molecular weight of the

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[7] Combustion analyses by Miss Margaret McCarthy and Miss Theta Spoor.

[8] Sudborough, *Ber.*, **27**, 514 (1894).

[9] Asinger, *J. prakt. Chem.*, **142**, 298 (1935).

[10] The value used for the molecular depression of the freezing point of *p*-nitrotoluene (m. p. 52°) was 7.77.

[11] Mol. wt. = $\eta_{sp}/Cgm \times 5.6 \times 10^{-4}$. See ref. 1.

[12] By wet oxidation with mixed silver and potassium dichromate in sulfuric acid. The bromine generated was absorbed in alkaline hydrogen peroxide according to Zazherl and Krainick (*Microchemie*, **11**, 61 (1932)) but analysis by Volhard titration of bromide ion in the absorbate was found to be more accurate than titration of excess alkali, evidently due to volatilization of organic acids.

recovered polymer (2450) (visc.) indicated only very slight degradation but the recovery of only 75% of the starting material suggests that the other 25% was degraded sufficiently to have remained in solution during purification by reprecipitation.

To test whether the oxygen might have entered the polymer by reaction with oxygen or peroxide in the dioxane during purification, a sample of oxygen-free polystyrene (3 g.) which had been prepared by the action of chloroacetyl peroxide on styrene at 95°[8], was dissolved in 100 cc. of ordinary dioxane which gave a positive test for peroxide with potassium iodide. After standing for three days exposed to air and sunlight, the polymer (2.9 g.) was recovered unchanged.

Anal. Before exposure: C, 91.54; H, 7.53; Cl, 1.05; mol. wt., 10,700 (visc.). After exposure: C, 91.14; H, 7.87; Cl, 1.01; mol. wt., 10,350 (visc.).

Summary

Polystyrene prepared with 3,4,5-tribromobenzoyl peroxide as catalyst has been found to contain bromine corresponding to about one tribromophenyl radical per polymer molecule. It has been shown that these tribromophenyl groups were acquired during the course of polymerization.

URBANA, ILLINOIS RECEIVED AUGUST 10, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Orientation of Molecules Produced Photochemically in Rigid Solvents

BY GILBERT N. LEWIS AND JACOB BIGELEISEN

It was recently discovered by Lewis and Lipkin[1] that when certain substances are irradiated in a rigid solvent by polarized light the molecules of the colored substances produced are so oriented that the absorption coefficients vary with the direction of polarization of the measuring light. This observation is not only of interest as offering the first instance of permanent dichroism[2] in a homogeneous solution, but it affords a valuable means of studying the relation between the structure of a molecule and its optical axes.

In the quasi-classical interpretation of absorption spectra that was developed by Lewis and Calvin[3] emphasis was placed not only upon the energies of electronically excited states but also upon the spatial direction of the oscillations of groups of electrons, which oscillations were assumed to characterize these excited states.[4]

All of the substances discussed in this paper are of the type illustrated in Fig. 1 in which, at least approximately, the structural formula is symmetrical with respect to a vertical line at the center. On grounds of symmetry, therefore, we must expect the direction of any electronic oscillation to be either parallel or perpendicular to such a line of symmetry.

Our experimental procedure has been to illuminate a colorless substance dissolved in a rigid medium, by a beam of plane polarized ultraviolet light, and then to examine the absorption of the colored sample produced, using measuring light polarized at various angles to the direction of polarization of the illuminating beam. Except in one case the illuminating and measuring beam were passed through the sample in the same direction. The details of the method will be described in the experimental section.

Normal Orientation: Tetramethyl- and *sym*-Diphenylbenzidine

In studying the phosphorescence of fluorescein in acid media it was shown[2] that the molecules in the phosphorescent state had a main optical axis for absorption in the same direction as that of the molecules in the ground state. Whenever in general this relationship holds between a parent molecule and the molecule produced from it by some photochemical process we shall speak of a

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(1) Lewis and Lipkin, THIS JOURNAL, **64**, 2801 (1942).

(2) Temporary dichroism, during the lifetime of the phosphorescent state, was found by Lewis, Lipkin and Magel, *ibid.*, **63**, 3005 (1941); **64**, 1774 (1942). Earlier, Weigert similarly obtained dichroism in adsorbed dyes (*Z. Physik*, **5**, 410 (1921)).

(3) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(4) In the theory of Lewis and Calvin the swinging of the entire cloud of mobile electrons is considered to be quantized as a whole. In a conjugated molecule which is long and nearly linear the electric oscillations are assumed to be along the molecule, that is, in the direction of high polarizability. The first electronic band (the band of lowest frequency) may be called the x band of the first order. This may be followed at a higher frequency (which would be twice the first frequency if the oscillations were harmonic) corresponding to an oscillation of higher amplitude in the same direction. This is the x band of the second order.

In a nearly planar molecule, which is not radially symmetrical, there is a unique direction of maximum polarizability. The first absorption band, again called the x band, will correspond to oscillations in that direction which will be called the main optical axis. The second absorption band may be a second order x band, but ordinarily will be a y band with oscillations perpendicular to those of the x bands and along the line of minimum polarizability in the plane. In the present paper we deal solely with x bands and, except in one instance, with x bands of the first order. We are going to show how the directions of electronic oscillation, or the optical axes, may be studied experimentally.