fluoride to yield isopropyl derivatives of phenol in both cases.

Evidence has been presented which indicates that the condensation of alcohols with phenol, especially propyl (*n*- and iso), takes place through the formation of an olefin as an intermediate and subsequent condensation with phenol.

NOTRE DAME, INDIANA RECEIVED DECEMBER 10, 1934

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Polymerization of Styrene, Citral and Heptaldehyde

BY HOWARD E. THOMPSON AND ROBERT E. BURK

This paper represents some observations on highly purified samples of styrene, citral and heptaldehyde in the presence and absence of oxygen.

Experimental

The chemicals used were Eastman C. P. grade. They were dried, distilled, fractionated and the middle third subjected to two or more distillations at a pressure of $<10^{-4}$ mm. of mercury. In the case of citral, purification, according to Dodge,[1] was carried out before the above treatment was given it. The styrene was always distilled over sodium just prior to its high vacuum distillation, and the mesitylene was repeatedly distilled over metallic sodium.

Heptaldehyde was studied first.[2] We sought to investigate in particular the relation between its oxidation and polymerization reactions. Two gas burets were connected by separate tubes to the inner curvature of a reniform reaction vessel of 10-ml. capacity. The latter was immersed in a thermostat and was mechanically shaken. The arrangement allowed a charge of oxygen in the burets to be passed back and forth through the sample in a uniform manner and without loss of the latter. The oxygen circulation was automatic.

The progress of the reaction was followed by diminution in the oxygen charge, and by analysis.

The high vacuum purification apparatus was of more or less conventional design. It contained no ground glass or rubber joints and was made of Pyrex and quartz. It was provided with a very efficient two-stage mercury condensation pump, McLeod gage, etc.

In experiments on the polymerization of styrene, this substance after purification was distilled into viscometers, dilatometers, etc., which were sealed to the high vacuum system during the filling and sealed off from it after filling. The capillary viscometers had a symmetrical shape and were as nearly alike as we could make them. All of these experiments were carried out at 44 ± 0.1°.

When mesitylene was used as a diluent for styrene, it was purified and sealed in weighed bulbs of various sizes. These were then sealed together with a heavy glass slug in an appendage to the vacuum viscometers, otherwise of the usual design. After filling the viscometer with styrene and sealing it off, the mesitylene bulb was broken, and the contents passed into the viscometer. The appendage was then sealed off.

Water was introduced by sealing pure hydrates (sodium sulfate decahydrate) in appendages of vacuum viscometers otherwise of the usual design. After filling the viscometer with styrene the requisite amount of water was obtained from the hydrate by warming and the appendage containing the residue sealed off.

Non-volatile catalysts were introduced directly into the vacuum viscometers and "degassed" before introducing styrene. Volatile catalysts were sublimed into the vacuum viscometers from an appendage.

Samples of heptaldehyde which were prepared by the high vacuum technique underwent no apparent change in sealed tubes over periods of some months. Samples of this material were investigated in the oxygen apparatus by Miss E. Jamison and H. P. Lankelma. They found that the drastic purification caused no observed deviation in the behavior of the heptaldehyde. No induction period was observed and the total amount of oxygen absorbed was one mole per mole of compound. This required twenty-four hours at 42°.

Citral polymerized in the same apparatus at 98° with the absorption of one-half mole of oxygen in twenty hours, which represented substantial completion of the reaction and a marked thickening of the citral. No induction period was observed.

Styrene at 118° in the same apparatus polymerized with the absorption of one-third mole of oxygen. The reaction was substantially complete in fifty-two hours, after which time the styrene had thickened markedly. An induction period of thirty minutes was observed.

It was thus found that in the case of citral and styrene polymerization dominated oxidation, whereas the contrary was true in the case of heptaldehyde.

Citral and styrene were then drastically purified in the high vacuum apparatus. The thus purified citral in a sealed tube of Corex glass was stable for more than three years. It survived a twenty-minute treatment with the full radiation from a new 220-volt, 1.5-amp. mercury arc at 30 cm. without visible change. Nor did heating for one hour at the temperature of boiling water produce a visible effect.[3]

The vacuum purified styrene, however, continued to polymerize, though at a somewhat diminished rate. While the dependence of the polymerization of citral upon

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[1] Dodge, *Am. Chem. J.*, **11**, 456 (1889).

[2] For greater detail, see H. E. Thompson's dissertation, Western Reserve University, June, 1934.

[3] Citral in the presence of oxygen at room temperature undergoes polymerization to a thick yellow liquid.

oxygen was evident, the similar dependence of the polymerization of styrene was left open since the merest traces of oxygen might be effective and peroxides distilling over with the styrene might be present.

A further study of the mechanism of the polymerization of styrene was then carried out. The rate was followed by viscosity changes using both falling ball and capillary viscometers, by mean molecular weight change, and by density changes. The influence of inhibitors, suspected catalysts, extension of surface, dilution, and deoxygenation with pyrophoric iron or alpha-naphthol was investigated.

Viscosity changes were substantially reproducible, and followed smooth curves. In order to compare different experiments in different viscometers, variations in volume of solvent and in capillary constants were eliminated by multiplying all efflux times by that factor which would reduce the initial efflux time to one.

It was then found that when the reaction time to reach a given viscosity was divided by the corresponding time in a standard experiment and all other reaction times for the given experiment multiplied by the same factor *k*, then practically all of the 32 curves coincided.

TABLE I

POLYMERIZATION OF STYRENE AT 44° IN VACUUM CAPILLARY VISCOMETERS

Expt.	*k*	Remarks
1	1.0 to 0.42	Pure styrene, arbitrarily selected as standard with $k = 1.0$
11	2.9	Dry air admitted to purified sample and then re-evacuated
12	1.5	Same
14	1.0	Very minute amount of air (see Expt. 11) plus small amount (0.1 in 200 very roughly) of α-naphthol
15	0.3	Small amount (about $^1/_{50}$ roughly) of water
16	.84	A much smaller amount of water than 15 (roughly $^1/_{200}$)
17	.82	Very small amount (roughly $^1/_{500}$) of α-naphthol
18	.88	Very small amount (roughly $^1/_{500}$) of α-naphthol
19	.66	A very small amount of α-naphthol (roughly $^1/_{500}$)
20	.024	α-Naphthol deoxidized and small amount (roughly $^1/_{50}$) of α-naphthol added
21	1.1	α-Naphthol deoxidized but nothing added
22	0.90	Same
23	.95	Pyrophoric iron deoxidized, 8-fold surface/volume ratio increase
24	.95	Pyrophoric iron deoxidized, 10-fold surface/volume ratio increase
25	1.4	Pyrophoric iron deoxidized
26	1.0	Same
27	0.7	Pure styrene, molecular weight tube
28	.74	Same

Binary mixtures: Mesitylene and Styrene

Expt.	*k*	Styrene, g.	Mesitylene, g.	Concn. of styrene
29	0.08	1.318	1.2254	0.519
30	.026	1.318	1.0988	.549
31	.126	1.318	0.4613	.744
32	.968	1.318	1.0284	.563

The experiments in which the concentration of styrene was varied, did not show sufficient regularity to enable the order of the reaction to be determined. The effect of the concentration factor appeared to be dominated by the effect of catalysts. In view of this it was not thought worth while to investigate the temperature coefficient.

The data obtained in capillary viscometers are summarized in Table I.

Extension of surface failed to increase the rate of viscosity change as shown by experiments 23 and 24.

In concurrent measurements of volume and viscosity by means of a combination dilatometer and falling ball viscometer, the density was found to be constant up to viscosities greater than those which were conveniently measurable in the capillary viscometer; but it increased eventually.

When a sample of styrene had polymerized to such an extent that the efflux times in the capillary viscometers had increased 200-fold, practically all of the styrene could be distilled out of the gel at 100° by cooling the other end of the viscometer. This left a small amount of fibrous polymer which did not appear to decompose until it charred on strong heating. This represented but a fraction of a per cent. of the styrene. On the other hand, that styrene which distilled out of the gel changed in viscosity some twenty times as fast as the original sample.

Molecular weights of some of the samples of styrene which had polymerized *in vacuo* were then determined by the freezing point method in benzene. In no case was any but a minor increase in molecular weight observed. The purified styrene in vacuum capillary viscometers at 44° underwent a change in viscosity at a velocity which varied from sample to sample by a factor of 2.5. However, the variation was by a factor of approximately 100 when accelerated by minute amounts of air on the one hand, or when inhibited by small amounts of alpha-naphthol on the other.

These observations are consistent with the mechanism that the polymerization of highly purified styrene results in relatively few large molecules. Such a result could occur if the reaction were catalytic, the catalyst remaining attached to the polymer during its growth.

This mechanism is further supported by the fact, shown in Table I, that certain compounds could inhibit the rate of viscosity change. This point is brought out in experiment 20 and by the effect of dilution with mesitylene where the catalytic effect exceeded any expected kinetic dilution effect.

In several instances during the course of polymerization of highly purified styrene *in vacuo*, the viscometer was immersed in liquid air for periods varying from three and one-half hours to thirty days. It was invariably found that on replacing the viscometers in the thermostat the normal prior rate of polymerization was resumed. This evidence is not favorable to a thermal chain mechanism for the reaction. Nor did the failure of highly purified citral to polymerize under the influence of heat, ultraviolet light, etc., encourage the acceptance of the chain hypothesis.

Upon admitting air to the vacuum system after distilling styrene in it, a pronounced whitish luminescence was often noticed near the points at which styrene bulbs had been sealed off. This occurred only at small air pressures.

This work would suggest that the greatest care should be exercised in attempting to correlate propensity to polymerize with molecular structure, since granting the possibility of polymerization, catalysts appear to be the more important factor.

Summary

The polymerization of highly purified styrene, citral, and heptaldehyde has been investigated in the presence of and substantial absence of oxygen.

Citral and heptaldehyde are stable in the substantial absence of oxygen. Styrene continues to polymerize under these conditions but at a diminished rate, This polymerization is probably still governed by catalysts. The effect of some catalysts and inhibitors has been investigated.

CLEVELAND, OHIO RECEIVED DECEMBER 12, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Tritylation of Sugar Mercaptals[1]

BY M. L. WOLFROM, JOSEPH L. QUINN AND CLARENCE C. CHRISTMAN

In view of the publication of Micheel and Spruck[2] on the triphenylmethyl (trityl) ether of galactose ethyl mercaptal, we wish to report the work completed in this Laboratory on the tritylation of a number of sugar mercaptals. The work herein reported was completed before the above article of Micheel and Spruck appeared and was also well under way before the appearance of the very important publication of Micheel and Suckfüll[3] on the action of mercuric chloride on 6-iodogalactose ethyl mercaptal tetraacetate. In the latter, the advantage of introducing halogen on the C_6 atom in connection with the synthesis of derivatives of the free aldehydo form was indicated, while the preferential substitution of halogen by the trityl group is shown in the former.

All compounds now reported were obtained in crystalline form and were recrystallized to constant melting point and rotation.

In 1886 Kiliani[4] commented on the Tollens' ring structure for *d*-glucose by stating that this conception would greatly complicate hexose structure because ring closure on any one of five carbon atoms was a possibility. This was forgotten until much later, when the furanose and pyranose ring structures were established. The partially substituted sugar mercaptals offer the possibility of studying other rings than the furanose and pyranose structures. The first study of this nature was made by Brigl and co-workers[5] who showed that glucose 3,4,5,6-tetrabenzoate exhibited no apparent tendency to react in an ethylene oxide structure and was an open chain or aldehydo form. This derivative was obtained by hydrolysis of the ethylmercapto groups from glucose ethyl mercaptal 3,4,5,6-tetrabenzoate. Micheel and Suckfüll[6] have now established a (1,6) or septanose ring structure for derivatives of *d*-galactose. These workers prepared 6-iodogalactose ethyl mercaptal tetraacetate and on hydrolyzing the ethylmercapto groups with mercuric chloride and cadmium carbonate in moist acetone, the iodine was also rather unexpectedly hydrolyzed with the formation of a galactose tetraacetate hydrate, which was apparently an aldehydo form. On further acetylation of this substance ring closure on the sixth carbon atom was effected and well proved.

The tritylation procedure of Helferich and coworkers[7] affords a convenient method for obtain-

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[1] A complete preliminary report of this work was published in THIS JOURNAL, **56**, 2789 (1934). The work herein recorded on the glucose compounds was reported completely at the 44th Meeting of the Ohio Academy of Science at Columbus, Ohio, March 30, 1934. Compounds I, II and III are recorded in the M.A. thesis of Mr. Clarence C. Christman, The Ohio State University, Dec. 15, 1933,

[2] F. Micheel and W. Spruck, *Ber.*, **67**, 1665 (1934).

[3] F. Micheel and F. Suckfüll, *Ann.*, **502**, 85 (1933).

[4] H. Kiliani, *Ber.*, **19**, 767 (1886).

[5] P. Brigl, H. Mühlschlegel and R. Schinle, *ibid.*, **64**, 2921 (1931).

[6] F. Micheel and F. Suckfüll, *Ann.*, **507**, 138 (1933); *Ber.*, **66**, 1957 (1933).

[7] B. Helferich and J. Becker, *Ann.*, **440**, 1 (1924).