[CONTRIBUTION FROM THE PETROLEUM AND CHEMICAL RESEARCH DEPARTMENT OF THE M. W. KELLOGG CO.]

The Chemistry of *p*-Xylylene. II. The Reaction of *p*-Xylylene with Oxygen

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Poly-*p*-xylylene peroxide is formed when oxygen is bubbled through a solution of *p*-xylylene. Homopolymerization, however, competes with peroxide formation, and a mixture of the two products sometimes is produced. When dry, the material decomposes explosively at *ca.* 100°. However, if the peroxide is dispersed in a liquid coolant such as water, the rate of decomposition is controlled easily and the danger of explosion is eliminated. Terephthalaldehyde, *p*-hydroxymethylbenzaldehyde, *p*-xylylene glycol and hydrogen are the only products of decomposition. The reaction is first order and the random scission of the peroxide bonds appears to be the rate-determining step. The activation energy and the frequency factor for the first-order rate constant are 34 kcal./mole and 4×10^{15} sec.$^{-1}$, respectively. The yield of terephthalaldehyde increases with temperature of decomposition to a maximum of *ca.* 90% at 125°.

Introduction

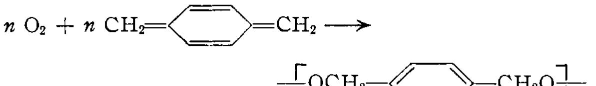
It was reported recently that a solution of *p*-xylylene can be prepared by a technique involving the fast flow pyrolysis of *p*-xylene at low pressure and subsequent instantaneous quenching of the pyrolysate directly into a solvent maintained at −78°.[2] Once prepared, these solutions are relatively stable at this temperature and have a half-life of about 21 hr.[2] Preliminary experiments have demonstrated the pseudodiradical behavior of *p*-xylylene and since oxygen is known to be a diradical,[3] the interaction of these two compounds was investigated.

Results and Discussion

When oxygen or air was bubbled through a freshly prepared solution of the monomer, the resulting precipitate contained a measurable amount of oxygen. The percentage of oxygen found therein was a function of the degree of agitation, rate of oxygen throughput, and polarity of the solvent. By utilizing all three variables to their maximum advantage at the optimum conditions, an addition product was obtained corresponding to an empirical formula of $(C_8H_8O_2)_n$. The rate of consumption of *p*-xylylene under these conditions was determined by the periodic iodometric titration of an aliquot sample of the solution and found constant (Fig. 1), despite the fact that the temperature of the solution was raised during the reaction from −78 to −44°. The actual rate, however, is dependent upon the throughput of oxygen. It was concluded, therefore, that the reaction is of zero order.

The precipitate corresponding to an empirical formula of $-(C_8H_8O_2)_n-$ is insoluble at room temperature in all available solvents and a decomposition occurs when the temperature is raised to about 100°. This instability prevented the determination of its molecular weight.

To elucidate its basic structure, the peroxide was decomposed in vacuum at 80 to 90°. The products of decomposition, which accounted for 95% of the original peroxide, were collected on a cold finger and found to be a mixture of aldehydes and alcohols. A small fraction of the mixture was oxidized by potassium dichromate and yielded terephthalic acid as the only product of oxidation. The remainder of the mixture was separated by chromatography. *p*-Xylylene glycol, *p*-hydroxymethylbenzaldehyde and terephthalaldehyde were the only compounds isolated. These results indicate that poly-*p*-xylylene peroxide is formed by the reaction



A large quantity of the polymeric peroxide, thoroughly dispersed in a tenfold amount of water, was then decomposed at reflux temperature over a period of 24 hours. A material balance, which accounted for 96% of the original material, proved that every mole of *p*-xylylene peroxide unit decomposed yielded 60% of terephthalaldehyde, 35% of *p*-hydroxymethylbenzaldehyde and 5% of *p*-xylylene glycol. Molecular hydrogen in 99% purity, as determined by mass spectrometric analysis, was collected during decomposition and the total quantity was roughly equivalent to the amount of terephthalaldehyde produced.

Although a large quantity of the peroxide can be decomposed safely when dispersed in a liquid medium, the same bulk of dry compound explodes violently when heated to *ca.* 100°. The peroxide, however, is stable at room temperature and can be stored for indefinite periods without any danger of decomposition.

By the proper control of oxygen throughput and of agitation of the *p*-xylylene solution, a series of peroxides was prepared with varying oxygen contents from 1 up to 23% (the corresponding average ratio of *p*-xylylene to oxygen was calculated to be 31 to 1 up to 1 to 1). These samples were decomposed in an aqueous slurry and in each case terephthalaldehyde, *p*-hydroxymethylbenzaldehyde, *p*-xylylene glycol and hydrogen were the only compounds isolated. The residual undecomposed material was essentially the α-form[4] of poly-*p*-xylylene containing only traces of carbonyl or hydroxy groups. Since no aldehydes or alcohols containing two or more phenyl groups were obtained, it is concluded that the structural composition of the peroxide is not that of poly-*p*-xylylene with oxygen distributed statistically along the chain, but rather that of a mixture of blocks of poly-*p*-xylylene and poly-*p*-xylylene peroxide.

The following mechanism for copolymerization is postulated in order to account for these results.

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(2) L. A. Errede and B. F. Landrum, THIS JOURNAL, **77**, 4952 (1957).

(3) R. S. Mulliken, *Phys. Rev.*, **32**, 880 (1928).

(4) C. J. Brown and A. C. Farthing, *J. Chem. Soc.*, 3270 (1953).

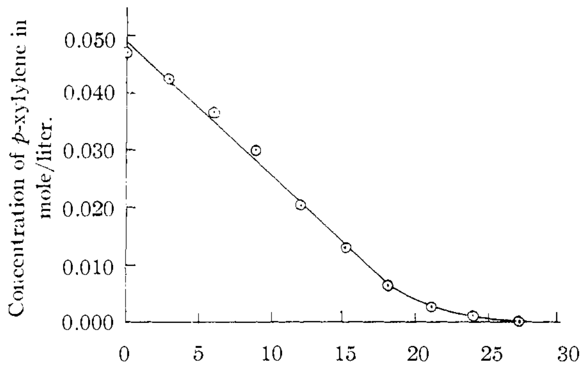

Fig. 1.—The addition of oxygen to *p*-xylylene.

The reaction is initiated by the rapid addition of oxygen.

$$\mathrm{M} + \mathrm{O_2} \longrightarrow \cdot\mathrm{MOO}\cdot$$

The *p*-xylyl radical then reacts faster with an oxygen radical than with a second monomer unit

$$\mathrm{O_2} + \cdot\mathrm{MOO}\cdot \longrightarrow \cdot\mathrm{OOMOO}\cdot$$

The peroxy radicals then combine with a monomer unit or a *p*-xylyl radical of a propagating peroxide chain.

$$\cdot\mathrm{OOMOO}\cdot + \mathrm{M} \longrightarrow \cdot\mathrm{OOMOOM}\cdot$$

$$\cdot\mathrm{OOMOO}\cdot + \cdot\mathrm{MO(OMO)}_m\mathrm{O}\cdot \longrightarrow \cdot\mathrm{O(OMO)}_n\mathrm{O}\cdot$$

The oxygen is consumed as rapidly as it is supplied. Copolymerization, therefore, occurs at or near the gas–liquid interphase.

Any oxygen or propagating peroxide chain which penetrates deep within the liquid phase where only monomer is present will initiate homopolymerization.

$$\cdot\mathrm{OOM}\cdot + n\,\mathrm{M} \longrightarrow \cdot\mathrm{M}_x\mathrm{OOM}_y\cdot$$

Since poly-*p*-xylylene peroxide is a non-volatile and insoluble solid material, it was impossible to study its isothermal decomposition in a homogeneous medium. Consequently, the investigation was carried out in a heterogeneous system in which the peroxide was decomposed while dispersed in a tenfold amount of water. The large volume of liquid served to maintain isothermal conditions and to assure the reproducibility of experimental conditions.

Previous workers[5] have shown that the rate-determining step for the decomposition of di-*t*-butyl peroxide and similar di-alkyl peroxides is the rupture of the O–O bond, and that subsequent reactions lead to a rather complex mixture of products such as methane, ethane, formaldehyde, ketones and alcohols.[6] Anomalously, in this case the reaction is relatively clean-cut and is not complicated by the formation of hydrocarbons and formaldehyde so long as isothermal conditions are maintained within the peroxide particles suspended in the aqueous coolant. The formation of two aromatic aldehyde groups and hydrogen or the formation of an aromatic aldehyde and an alcohol are the only two over-all reactions of importance that ensue the initial thermal rupture of the O–O bond. If these alternative routes are concurrent reactions, then the rate of hydrogen evolution is directly proportional to the rate of O–O bond rupture and can be used, therefore, to measure the rate of decomposition. Hence, the first-order rate constant k is given by the equation

$$\ln(1 - V/V_0) = -kt$$

where V is the volume of hydrogen liberated at time t, and V_0 is the total volume of hydrogen liberated.

A series of degradation studies was made in which the volume of hydrogen liberated was recorded as a function of time and of temperature of decomposition. The results are summarized in Fig. 2. It is seen that within the temperature range 80 to 100° the kinetics of poly-*p*-xylylene peroxide decomposition is first order. The log of the experimentally determined specific rate constants was plotted as a function of the reciprocal of the corresponding absolute temperatures of decomposition and a straight line relationship was obtained. Hence, the rate constant for *p*-xylylene peroxide degradation is expressed as

$$k = 4 \times 10^{15}\, e^{(-34\ \mathrm{kcal.}/RT)}$$

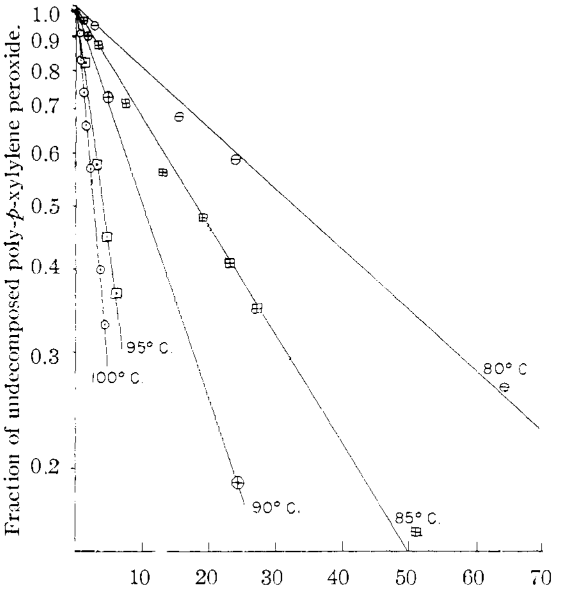

Fig. 2.—Rate of decomposition of poly-*p*-xylylene peroxide dispersed in water as a function of temperature of decomposition.

The results obtained in this study are compatible with the postulated mechanism shown in Fig. 3. The rate determining step (k_1) of the isothermal heterogeneous decomposition of the polymeric peroxide is the rupture of the O–O bond. This occurs in a random fashion and is not followed by a "zipper-like" decomposition. The over-all ensuing reactions (k_2 and k_3), which involve the two aralkoxy radicals formed by the rupture of the peroxide bond, occur so rapidly that the ultimate products,

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[5] W. E. Vaughan, F. F. Rust and J. H. Raley, This Journal, **70**, 88 (1948); F. F. Rust, F. H. Seubold and W. E. Vaughan, *ibid.*, **72**, 338 (1950).

[6] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 63–72.

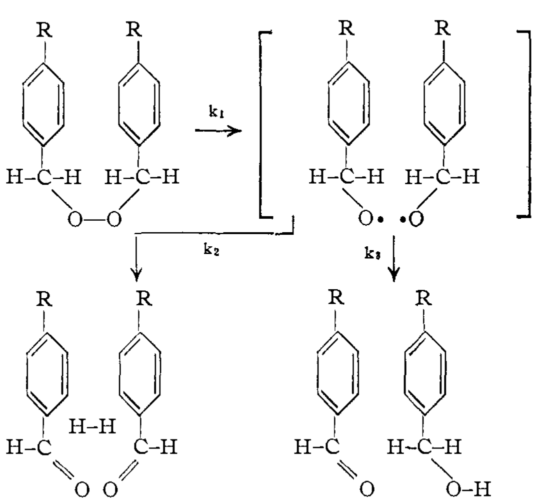

Fig. 3.—Mechanism of decomposition of poly-p-xylylene peroxide dispersed in water.

aldehydes and molecular hydrogen or aldehyde and alcohol, are formed before the two *para*-substituted alkoxy radicals have an opportunity to separate. The heat of reaction is absorbed by the aqueous medium and energy transfer through the polymeric chain to an adjacent peroxide bond does not occur. The over-all reaction sequence is; therefore, postulated to take place in a "cage"[7] as indicated in Fig. 3.

The yield of terephthalaldehyde obtained *via* the thermal degradation of poly-p-xylylene peroxide dispersed in water was studied as a function of temperature of decomposition. The results are summarized in Table I and Fig. 4. The yield of terephthalaldehyde increases from 20% at 65° to a maximum of *ca.* 90% at 125°. The decrease in yield of terephthalaldehyde at still higher temperatures of decomposition is caused by the inadequate rate of dissipation of energy within the relatively large particle of insoluble poly-p-xylylene peroxide. Under these conditions, the overheating leads to an uncontrolled decomposition and degradation which complicate the reaction. The maximum yield of terephthalaldehyde is increased to about 95% at 130° if the polymer is powdered before decomposition. This was not used in general practice, however, because of the danger of explosion during grinding.

Below 130°, the formation of terephthalaldehyde and p-hydroxymethylbenzaldehyde account for 90 to about 100% of the three non-volatile products of the decomposition. Consequently, the ratio of the specific rate constant for the formation of molecular hydrogen and two aldehyde groups (k_2) to the specific rate constant for the formation of one aldehyde and one alcohol group (k_3) is given by the corresponding ratio of yield of terephthalaldehyde to yield of p-hydroxymethylbenzaldehyde.

$$\frac{k_2}{k_3} = \frac{\text{yield of terephthalaldehyde}}{100 - \text{yield of terephthalaldehyde}}$$

The log of this ratio was plotted as a function of the reciprocal of the absolute temperature of decomposition (Fig. 5) and the difference in the activation energies for the two reactions ($E_2 - E_3$) was thus determined to be 13 kcal.

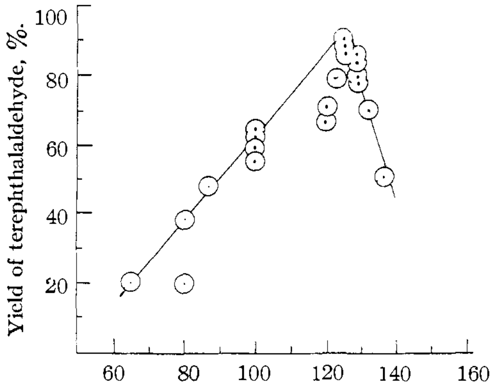

Fig. 4.—Yield of terephthalaldehyde obtained *via* decomposition of poly-p-xylylene peroxide dispersed in water as a function of temperature of decomposition.

Experimental

Poly-p-xylylene Peroxide.—A clear solution of p-xylylene at −78° was prepared as described previously.[2] The solution was protected from atmospheric oxygen until the very instant copolymerization was to be initiated. At this moment oxygen or air was introduced at such a rate that the contents of the flask was converted to a violently agitated mass of bubbles.

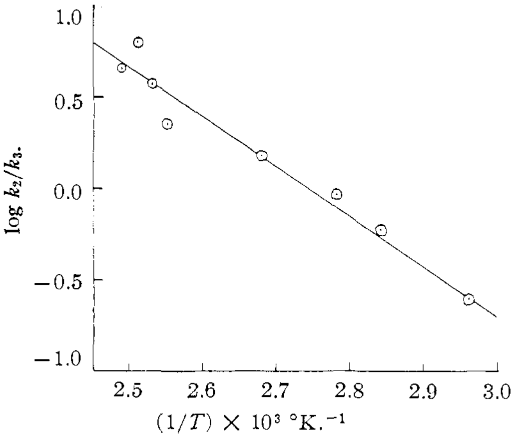

Fig. 5.—Log of the ratio of k_1, the specific rate constant for aldehyde plus hydrogen formation, to k_2, the specific rate constant for aldehyde plus alcohol formation, as a function of the reciprocal of the absolute temperature of decomposition.

The addition of oxygen was interrupted periodically in order to determine the concentration of unreacted p-xylylene and a 25-cc. aliquot sample was removed by means of a rapid delivery pipet that had been pre-chilled to −78°. The sample was added to a known excess of iodine dissolved in CCl_4. The solution was warmed to room temperature and the excess iodine was back titrated with aqueous $Na_2S_2O_3$. Vigorous agitation was used throughout the titration and the end-point was indicated by the disappearance of the familiar iodine in CCl_4 color. At the end of the reaction, the mixture was warmed to room temperature and a final aliquot taken for use as a blank.

Poly-p-xylylene peroxide precipitated from solution in a very finely divided although swollen state. The insoluble product was removed by filtration. The filter cake resembled "butterscotch pudding" in its physical appearance. It was slurried in acetone and recollected by filtration in order to remove adsorbed impurities. The yield of p-

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[7] M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

TABLE I

YIELD OF TEREPHTHALALDEHYDE AS A FUNCTION OF TEMPERATURE OF DECOMPOSITION OF POLY-*p*-XYLYLENE PEROXIDE SUSPENDED IN WATER

Condition of decomposition Temp., °C.	Time	Yield of terephthalaldehyde, %	Ratio of moles terephthalaldehyde to moles of hydrogen
65	7 days	20	0.67
80	7 days	20	..
80	4 hr.	38	.82
87	6 days	48	.73
100	3 days	55	..
100	24 hr.	59	.86
100	24 hr.	63	..
100	18 hr.	64	.61
120	18 hr.	67	.91
120	18 hr.	71	.95
123	18 hr.	79	..
125	18 hr.	90	1.09
125	18 hr.	86	..
125	2 hr.	87	1.25
129	18 hr.	78	0.92
129	18 hr.	86	1.12
129	3 hr.	84	1.09
129	1.5 hr.	78	0.89
132	18 hr.	70	.96
136	3 hr.	51	.71

xylylene peroxide based upon available monomer, as determined by iodometric titration, was almost quantitative. *Anal.* Calcd. for $(C_8H_8O_2)_n$: C, 70.57; H, 5.92. Found: C, 70.5; H, 5.73.

Decomposition of Poly-*p*-xylylene Peroxide under Vacuum and Subsequent Identification of the Resulting Products.—Poly-*p*-xylylene peroxide was carefully powdered and passed through a 40-mesh screen. The powder (8 g.) was spread evenly across the bottom of a 1-liter vacuum filtration flask which was fitted with a cold finger. The flask was evacuated and the bottom warmed in a water-bath at 80–90°. Decomposition was allowed to occur over a period of 16 hr., at the end of which only a trace amount of non-volatile tarry products remained. The white crystalline sublimate (7.8 g.) was removed from the cold finger and found to be a mixture of aromatic alcohols and aldehydes. A 3-g. sample was oxidized at 100° using 10 g. of $K_2Cr_2O_7$ dissolved in 140 cc. of 15% aqueous H_2SO_4. The mixture was cooled to room temperature and the terephthalic acid obtained was removed by filtration. The compound, which did not melt below 300°, was identified by conversion to corresponding dimethyl ester (m.p. 138–139°).

The remaining 5-g. fraction of the alcohol aldehyde mixture was dissolved in a large volume of benzene and separated by chromatography. These compounds were isolated: terephthalaldehyde (m.p. 113–114°), *p*-hydroxymethylbenzaldehyde (m.p. 41.5–42.0°. *Anal.* Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.82. Found: C, 70.1; H, 5.35), and *p*-xylylene glycol (m.p. 117.0–117.5°. *Anal.* Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.29. Found: C, 69.6; H, 6.67). Final identification was made by conversion to the corresponding derivatives as described below.

Terephthalaldehyde (0.3 g.), m.p. 113–114°, was added to 1.5 g. of hydroxylamine hydrochloride dissolved in 10 cc. of water. To this was added 10 cc. of 10% NaOH and the mixture was agitated gently. The dilute basic solution was acidified and the insoluble dioxime was removed by filtration. The compound was recrystallized from hot water in the form of small white crystals (m.p. 214–215°).

p-Hydroxymethylbenzaldehyde (1 g.) was added to an excess of hydroxylamine hydrochloride dissolved in 5 cc. of water. To induce crystallization the solution was frozen and then allowed to warm to room temperature. The white solid was removed by filtration and recrystallized from benzene to yield a half gram of *p*-hydroxymethylbenzaldoxime (m.p. 120–121°). *Anal.* Calcd. for $C_8H_9O_2N$: C, 63.52; H, 5.95; N, 9.27. Found: C, 63.42, 63.56; H, 6.20, 6.04; N, 9.02, 9.18.

p-Hydroxymethylbenzaldehyde (1.7 g.) was added to 3 g. of semicarbazine hydrochloride and 4.5 g. of sodium acetate dissolved in 30 cc. of water. The reaction mixture was warmed in a steam-bath for 10 minutes and then allowed to cool to room temperature. The white precipitate was removed by filtration and recrystallized from hot water to yield 3.5 g. of white crystals (m.p. 193–197°). The compound was then recrystallized from ethanol and the semicarbazone was obtained as white platelets (m.p. 196–197°).

p-Xylylene glycol (1 g.) was warmed with concentrated hydrochloric acid over a steam-bath for one hour. The insoluble *p*-xylylene dichloride was removed by filtration and recrystallized from hexane in the form of pearl-white platelets (m.p. 95–97°).

Decomposition of Poly-*p*-xylylene Peroxide–Poly-*p*-xylylene Mixtures in Water at or below 100°.—The weighed amount (5 to 250 g.) of poly-*p*-xylylene peroxide and poly-*p*-xylylene mixture was suspended in a tenfold amount of water and the isothermal decomposition was studied in a closed system. The hydrogen evolved was collected by water displacement and volume was recorded as a function of time. The hot reaction mixture was separated by filtration and the residue was re-extracted with hot water. The hot aqueous extracts were combined and allowed to cool to room temperature. Terephthalaldehyde was obtained as long, white, flat needles (m.p. 112–114°). The water-insoluble non-oxygen containing products were weighed as poly-*p*-xylylene; *p*-hydroxymethylbenzaldehyde and *p*-xylylene glycol were recovered from the mother liquor by continuous extraction with ether. The former was removed in the first few hours as an oil, whereas several days were required to recover the latter. The glycol was recrystallized once from benzene and the aldehyde alcohol from hexane. The percentage of poly-*p*-xylylene peroxide present in the original mixture was determined on the basis of weight difference of polymeric material before and after decomposition. The percentage yield of terephthalaldehyde was calculated on the basis of available peroxide. The results are summarized in Table I.

Decomposition of Poly-*p*-xylylene Peroxide above 100°.—Five grams of a mixture of poly-*p*-xylylene peroxide and poly-*p*-xylylene together with 50 cc. of water was placed in a glass-lined, 250-cc. Aminco bomb. The bomb was sealed and placed in a constant temperature bath which had been set at the indicated temperature of decomposition. The degradation reaction was allowed to occur over the recorded time interval. The bomb was then withdrawn from the bath and cooled to room temperature. The accumulated hydrogen was metered into a graduated receiver. The decomposition mixture was heated to redissolve the terephthalaldehyde and the resulting aqueous mixture was treated as described above. The results are summarized in Table I.

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