1,2-dimethoxyethane (distilled from lithium aluminum hydride) was added sodium (4.6 g., 0.2 g.-atom). A vigorous evolution of hydrogen resulted. To the stirred solution was added sodium trichloroacetate (35.0 g., 0.188 mole) and the mixture was refluxed with stirring for 1 hr., during which time a tan solid separated. A vigorous evolution of carbon dioxide occurred. The mixture was filtered hot and the residual solid (24.6 g.) was washed with hot 1,2-dimethoxyethane. On partial concentration and cooling crystals separated from the red-brown filtrate. The sodium salt (II), 12.5 g., 52% yield based on 3 moles of I to yield 1 mole of II, was filtered and recrystallized from ethanol, m.p. 274–276°. The infrared spectrum was identical to the spectra of II produced in the bromoform and chloroform reactions.

Anal. Calcd. for $C_{15}H_{21}O_8Na$: C, 51.11; H, 6.01. Found: C, 51.04; H, 6.28.

The salt (II) was shaken with dilute hydrochloric acid and ether until the yellow color disappeared. The ether extract was washed with water and the ether was evaporated using a Rinco evaporator. The product was dried over anhydrous sodium sulfate and pumped under a pressure of 0.3 mm. to remove traces of ether. The infrared spectrum of this tetraester was identical to that of the free ester prepared under these conditions from the product of the chloroform–sodium ethoxide run above.

(d) **Reaction of I with Chloroform.**—To a solution of diethyl malonate (32.0 g., 0.2 mole) in 100 ml. of 1,2-dimethoxyethane (distilled from lithium aluminum hydride) was added sodium (4.6 g., 0.2 g.-atom). A vigorous evolution of hydrogen occurred. To the stirred solution chloroform (12.0 g., 0.1 mole) was added dropwise. The mixture was refluxed for 16 hr., during which time a yellow solid separated. The mixture was filtered while hot and the residual solid (9.0 g.) was washed with hot 1,2-dimethoxyethane. On concentration and cooling crystals deposited from the filtrate. The salt (II), 12.0 g., 14% based on 4 moles of I to yield 1 mole of II, was filtered and recrystallized from ethanol, m.p. 274–276°. The infrared spectrum was identical to the spectra of the samples previously isolated.

(e) **Reaction of I with Ethyl Trichloroacetate–Sodium Methoxide.**—To a solution of diethyl malonate (32.0 g., 0.2 mole) in 75 ml. of 1,2-dimethoxyethane (commercial grade) was added sodium (4.5 g., 0.2 g.-atom). A vigorous evolution of hydrogen occurred. The solution was cooled to 0° and sodium methoxide (5.4 g., 0.1 mole) was added. To the stirred mixture ethyl trichloroacetate (19.2 g., 0.1 mole) was added dropwise. A muddy brown precipitate formed immediately. The reaction mixture was stirred for 8 hr. at 0°. The mixture was filtered and the filtrate was evaporated to dryness with a Rinco evaporator. The residue was extracted in a Soxhlet extractor for 24 hr. (ethanol) and yielded II (6.0 g., 17% based on acetate). The infrared spectrum was identical to that of the above products.

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The Decomposition of Perortho Esters

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The synthesis of α,α-dimethoxy-α-*t*-butylperoxytoluene (I), α,α,α′,α′-tetramethoxy-α,α′-di(*t*-butylperoxy)-*p*-xylene (II), and α,α,α′,α′-tetramethoxy-α,α′-di(*t*-butylperoxy)-*m*-xylene (III) from the related methyl ortho esters and *t*-butyl hydroperoxide is described. The thermal decomposition of these perortho esters in both cumene and *t*-butylbenzene lead to *t*-butoxy and substituted α,α-dimethoxybenzyloxy radicals. The latter fragment to methyl arylcarboxylates and methoxy radicals about ten times more readily than the competitive fragmentation to dimethyl carbonate and aryl free radicals.

The thermal decomposition of peresters, RCO_3R', has been well established as a source of free radicals capable of initiating vinyl polymerization.[1] The kinetics of decomposition indicate that homolysis of either the O—O bond alone[2] or both O—O and R—C bonds simultaneously are occurring, depending on the nature of R.[3] In contrast, much less is known about perortho esters, $RC(OR')_2$-OOR''.[4] These have been prepared by autoxidation of acetals,[5,6] by transesterification of ortho esters with hydroperoxides[7] and more recently, by the addition of hydrogen peroxide to ketene acetals[8]; however, no studies of their thermal decomposition have been reported. In this work, the synthesis and decomposition of three perortho esters, α,α-dimethoxy-α-*t*-butylperoxytoluene (I), α,α,α′,α′-tetramethoxy-α,α′-di(*t*-butylperoxy)-*p*-

I

II

III

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[1] (a) N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 642 (1946); (b) R. P. Perry and K. P. Seltzer, *Modern Plastics*, **25**, No. 3, 134 (1947).

[2] (a) A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408 (1951); (b) A. T. Blomquist and I. A. Bernstein, *ibid.*, **73**, 5546 (1951).

[3] P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

[4] R, R′ = alkyl or aryl. R″ = alkyl, aryl, or $RC(OR')_2$—. Perortho esters containing more than one peroxide group per ortho ester function are unknown.

[5] M. Lederer, dissertation, Karlsruhe (1950).

[6] A. Rieche, E. Schmitz, and E. Beyer, *Chem. Ber.*, **91**, 1935 (1958).

[7] A. Rieche, E. Schmitz, and E. Beyer, *ibid.*, **91**, 1942 (1958).

[8] A. Rieche, E. Schmitz, and E. Grundemann, *Angew. Chem.*, **72**, 635 (1960).

xylene (II), and α,α,α′,α′-tetramethoxy-α,α′-di-(*t*-butylperoxy)-*m*-xylene (III) is described.

Results

The perortho esters I, II, and III were prepared by heating the appropriate methyl ortho ester with two to four equivalents of *t*-butyl hydroperoxide for each ortho ester group in *n*-hexane and distilling the liberated methanol as its azeotrope with *n*-hexane. The use of catalytic amounts of toluenesulfonic acid or Dowex 50 sulfonic acid resin seemed to offer no improvement in yield. Below 100°, the *t*-butyl peroxy ortho esters do not decompose appreciably and are stable for several months at 0°. While they all oxidize acidified sodium iodide solutions, this reaction could not be used for their quantitative determination. A number of iodometric techniques[2a,9] all gave values which were erratic and inconsistent with the proposed structures. Similar difficulties with *t*-butyl peresters have been described by others and attributed to acid-catalyzed rearrangement of the peresters.[1a,8] The identity of the perortho esters was based on the synthetic path, the elementary analysis, and the character and quantity of the decomposition products. The purity was established by inspection of the infrared spectrum for carbonyl and hydroxyl absorption, characteristic of the expected impurities.

The decomposition of perortho esters I, II, and III in pure cumene and *t*-butylbenzene at 150.0° evolved gases which were shown by mass spectrometry to be mainly methane and carbon monoxide. While the rate of gas evolution followed no integral kinetic order, an approximation of the rate of peroxide decomposition based on the rate of gas evolution leads to the graphically determined half-lives shown in Table I. For comparison, the extrapolated[2a] half-life for the decomposition of *t*-butylperbenzoate in *p*-chlorotoluene at 150° is 4.4 minutes.

TABLE I

GAS EVOLUTION FROM *t*-BUTYL PEROXY ORTHO ESTERS[a] AT 150°

	Cumene		*t*-Butylbenzene	
	Total mmoles	$t_{1/2}$, min.[b]	Total mmoles	$t_{1/2}$, min.[b]
I	1.46	22	2.33	24
II	1.20, 1.15	17, 16	2.60, 2.35	27, 33
III	0.94	27	1.35[c]	32

[a] 6 mmoles of peroxygen bonds in 300 mmoles solvent. [b] Time required for one half of total gas evolution. [c] 5.54 mmoles of peroxygen bonds in 300 mmoles solvent.

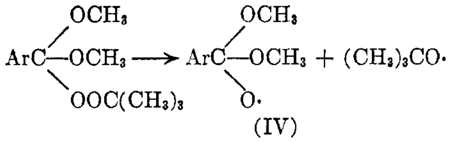
The efficacy of *t*-butyl perortho esters as initiators for vinyl polymerization is indicated by the fact that methyl methacrylate containing 0.11 mole per cent peroxygen as II gives an 8% yield of polymethyl methacrylate of average molecular weight 2.73 × 10^6 under conditions where monomer alone gave 2.0% polymer of average molecular weight 4.24 × 10^6.

Perortho esters I, II, and III were decomposed in both cumene and *t*-butylbenzene as indicated in Table II. Gases were analyzed by mass spectrometry; liquid and solid products were identified and determined by vapor phase chromatography (VPC) using known compounds as standards. Formaldehyde, which was formed in the decompositions, polymerized to paraformaldehyde and condensed on the walls of the condenser; determination was as the 2,4-dinitrophenylhydrazone. Isobutylbenzene, which had been formed by isomerization of the solvent in the decomposition of I in *t*-butylbenzene, was quantitatively determined by infrared analysis of the distilled solvent fraction. With I and II, product balances are in good agreement with the proposed structures. Perortho ester III, which had been isolated by molecular distillation, gave poorer material balances, due at least in part to the lower purity of the initial perortho ester. Two unidentified peaks in the VPC of the decomposition products, with retention times suggesting the *p*-carbomethoxyphenyl derivatives of cumene and *t*-butylbenzene, were also apparent. In any event, the products identified indicate the major course of the decomposition.

Discussion

The two O—O bonds in the disubstituted aromatic perortho esters II and III are sufficiently well insulated from each other so that there is no direct tautomeric way in which homolysis of one O—O bond can induce homolysis of the other. In this regard, II and III are simply difunctional examples of α,α-dimethoxy-α-*t*-butylperoxytoluene (I); their mode of decomposition can most conveniently be discussed in terms of the monosubstituted aromatic perortho ester.

The products of decomposition of I can readily be accounted for by the following scheme:



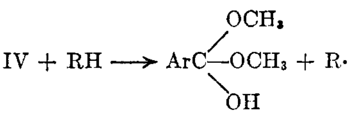
$$\mathrm{ArC(OCH_3)_2OOC(CH_3)_3} \longrightarrow \mathrm{ArC(OCH_3)_2O\cdot} + \mathrm{(CH_3)_3CO\cdot} \quad (1)$$

(IV)

$$\mathrm{(CH_3)_3CO\cdot} + \mathrm{RH} \longrightarrow \mathrm{(CH_3)_3COH} + \mathrm{R\cdot} \quad (2)$$

$$\mathrm{(CH_3)_3CO\cdot} \longrightarrow \mathrm{CH_3\cdot} + \mathrm{CH_3COCH_3} \quad (3)$$

$$\mathrm{CH_3\cdot} + \mathrm{RH} \longrightarrow \mathrm{CH_4} + \mathrm{R\cdot} \quad (4)$$



$$\mathrm{IV} + \mathrm{RH} \longrightarrow \mathrm{ArC(OCH_3)_2OH} + \mathrm{R\cdot} \quad (5)$$

(V)

$$\mathrm{V} \longrightarrow \mathrm{Ar\dot{C}O_2CH_3} + \mathrm{CH_3OH} \quad (6)$$

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[9] (a) F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Treseder, and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949). (b) C. D. Wagner, R. H. Smith, and E. D. Peters, *Ind. Eng. Chem.* (*Anal. Ed.*), **19**, 976 (1947). (c) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

TABLE II

DECOMPOSITION PRODUCTS OF PERORTHO ESTERS AT 150°, MOLES/MOLE OF PERORTHO ESTER

	I		II		III	
	Cumene[a]	*t*-Butylbenzene[a]	Cumene[b]	*t*-Butylbenzene[b]	Cumene[b]	*t*-Butylbenzene[c]
Carbon monoxide	0.00	0.08	0.00	0.16	0.00	0.12
Methane	.24	.30	.38	.62	.30	.36
Formaldehyde	[d]	[d]	.16	.15	[d]	[d]
Acetone	0.18	0.48	.38	.90	0.22	0.39
Methanol	.71	.63	1.23	1.19	.98	.98
t-Butyl alcohol	.79	.50	1.49	0.95	.87	.75
Dimethyl carbonate	.12	.07	0.26	.23	.17	.12
Benzene	.08	.03				
Methyl benzoate	.84	.96	.12	.30	.09	.13
Dimethyl terephthalate			.68	.77		
Dimethyl isophthalate					.50	.48
Dicumyl	.71		1.41		.99	
Isobutylbenzene		.26		[d]		[d]
t-Butyl alcohol/acetone	4.25	1.02	3.95	1.06	4.01	1.90
% Balance						
Aromatic	92	99	80	107	59	61
t-Butoxy[e]	97	98	93	92	55	57
Methoxy[f]	90	91	84	95	60	61

[a] Six mmoles in 300 mmoles of solvent. [b] Three mmoles in 300 mmoles of solvent. [c] 2.77 mmoles in 300 mmoles of solvent. [d] Present but not determined. [e] Acetone and *t*-butyl alcohol. [f] Methanol, carbon monoxide, formaldehyde, and methyl esters.

$$\text{IV} \longrightarrow \text{Ar}\cdot + (\text{CH}_3\text{O})_2\text{CO} \qquad (7)$$

$$\text{Ar}\cdot + \text{RH} \longrightarrow \text{ArH} + \text{R}\cdot \qquad (8)$$

$$\text{Ar}\cdot + \text{RH} \longrightarrow \dot{\text{Ar}}\text{RH} \xrightarrow{\text{R}\cdot} \text{ArR} + \text{RH} \qquad (9)$$

$$\text{IV} \longrightarrow \text{ArCO}_2\text{CH}_3 + \text{CH}_3\text{O}\cdot \qquad (10)$$

$$\text{CH}_3\text{O}\cdot + \text{RH} \longrightarrow \text{CH}_3\text{OH} + \text{R}\cdot \qquad (11)$$

$$\text{CH}_3\text{O}\cdot + \text{R}\cdot \longrightarrow \text{CH}_2\text{O} + \text{RH} \qquad (12)$$

$$\text{CH}_3\text{OH} \xrightarrow{\text{R}\cdot} \text{RH} + \cdot\text{CH}_2\text{OH} \xrightarrow{\text{R}\cdot} \text{RH} + \text{CH}_2\text{O} \qquad (13)$$

$$\text{CH}_2\text{O} \xrightarrow{\text{R}\cdot} \text{RH} + \dot{\text{C}}\text{HO} \xrightarrow{\text{R}\cdot} \text{RH} + \text{CO} \qquad (14)$$

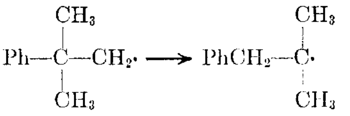
$$2\text{R}\cdot \longrightarrow \text{RR} \qquad (15)$$

While most of the steps in the reaction sequence are conventional, several warrant special consideration.

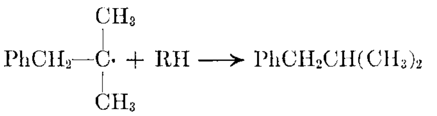
The primary step in the decomposition is no doubt the unimolecular scission of the peroxygen bond (equation 1) to give *t*-butoxy radicals and IV. A wholly concerted process in which either the Ar—C bond or the CH_3O—C bond is broken in the rate-determining step is not likely, since methyl benzoate and dimethyl carbonate, products from both of these cleavages, are observed. Further, it has been shown that the stabilities of the incipient free radicals are important in the transition state of such concerted decompositions. The phenyl-C bond is not broken in the transition state for the decomposition of *t*-butyl perbenzoate[3]; little is known about concerted CH_3O—C cleavage, although thermochemical data indicate that the methoxy radical is considerably more stable than the phenyl radical.[10]

The higher than usual[11] *t*-butyl alcohol/acetone ratios reported here are probably due to the hydrogen-donating abilities of the methoxy radical (equation 12), methanol (equation 13), and formaldehyde[12] (equation 14), which are also present.

The intervention of solvent as a source of hydrogen atoms is indicated by the dimerization of α-cumyl radicals to dicumyl in high yield in cumene solvent (equation 15). While no analogous dimers were detected in *t*-butylbenzene, the formation of the neophyl radical by hydrogen abstraction is indicated by the presence of isobutylbenzene, a product of its rearrangement (equations 16 and 17).



$$\text{Ph—C(CH}_3)_2\text{—CH}_2\cdot \longrightarrow \text{PhCH}_2\text{—C}(\text{CH}_3)_2\cdot \qquad (16)$$



$$\text{PhCH}_2\text{—C}(\text{CH}_3)_2\cdot + \text{RH} \longrightarrow \text{PhCH}_2\text{CH}(\text{CH}_3)_2 \qquad (17)$$

This isomerization has recently been reported in the decomposition of di-*t*-butyl peroxide in *t*-butylbenzene.[13]

The fate of radical IV is less clear and several possibilities arise. The α,α-dimethoxybenzyloxy radical (IV, Ar = phenyl) can abstract hydrogen directly to give the hypothetical intermediate V, which would undoubtedly decompose by a nonradical path to methyl benzoate and methanol (equations 5 and 6). Alternatively, IV may decompose by a free radical path to methyl benzoate and methoxy radicals, ultimately appearing as methanol (equations 10 and 11). If methyl benzoate is formed by the nonradical path (equations 5 and 6), it should be formed in greater amount

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(10) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(11) A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956).

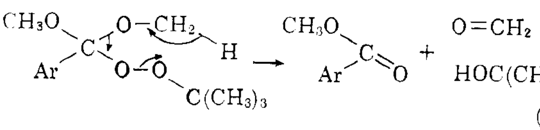
(12) Y. Takezaki and C. Takeuchi, *J. Chem. Phys.*, **22**, 1527 (1954).

(13) H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2921 (1960).

in cumene than in t-butylbenzene due to facilitation of the hydrogen abstraction reaction. That more methyl benzoate is formed in t-butylbenzene than in cumene invalidates equations 5 and 6 as the only route to methyl benzoate.

Perhaps the most striking reaction available to IV is the necessarily free radical scission to phenyl radicals and dimethyl carbonate (equation 7) which occurs to the extent of 6–13% per peroxygen bond for the various perortho esters in the two different solvents. By comparison, the cumyloxy radical from the decomposition of dicumyl peroxide in cumene at 138° gives only acetophenone and methyl radicals on fragmentation,[14] with no evidence for benzene and acetone.

The presence of dimethyl carbonate suggests the occurrence of equation 7, the existence of IV, and consequently the concurrent fragmentation of IV to methyl benzoate and methoxy free radicals. A simple thermochemical calculation, the validity of which has recently been discussed,[15] allows one to partition the two alternatives (equations 7 and 10). Using 69, −137.1, −71.7, and −0.5 kcal./mole as the enthalpies of formation (g, 25°, 1 atm.) of phenyl radicals, dimethyl carbonate, methyl benzoate, and methoxy radicals, respectively,[10] calculations indicate that equation 10 is more exothermic than equation 7 by 4.1 kcal./mole, so that if IV has sufficient life time to fragment to phenyl radicals and dimethyl carbonate, the concurrent fragmentation to methyl benzoate and methoxy radicals should predominate, as is borne out by experiment. Formaldehyde, methanol, and carbon monoxide are ultimate products of reactions of methoxy radicals, equations 11, 12, 13, and 14. It is also possible to visualize intramolecular processes leading to formaldehyde. A cyclic process indicated in equation 18[16] not only accounts for formaldehyde formation but also accounts for the high t-butyl alcohol/acetone ratios and poor initiation efficiency of t-butyl perortho esters. The formation of formaldehyde by intramolecular hydrogen abstraction by IV (equation 19) is not very likely.



(18)

(19)

(VI)

The radical VI would appear as acid or aldehyde, neither of which were detected. Further, it has been shown[17,18] that intramolecular abstraction of primary hydrogen by alkoxy radicals does not occur in quasi-five-membered transition states.

Experimental[19]

Methyl Orthobenzoate.—The procedure of McElvain and Venerable[20] was used. Distillation through a 36-in. spinning band column gave a chloride-free liquid, b.p. 114°/25 mm., n^{25}_D 1.4865 lit.,[20] b.p. 114–115°/25 mm., n^{25}_D 1.4858.

Methyl Orthoterephthalate.—$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-Hexachloro-$p$-xylene (Diamond Alkali Co.), 157 g. (0.50 mole) and a sodium methoxide solution prepared from 75 g. of sodium metal (3.25 g.-atoms) in 1200 ml. of dry methanol were heated for 5 hr. at 200° in a 4.5-l. stainless steel rocker bomb. The reaction mixture was filtered, the methanol evaporated, and the residual paste poured onto 1.5 l. of water and extracted with five 200-ml. portions of chloroform. The chloroform extracts were washed with saturated sodium bicarbonate solution, dried over anhydrous potassium carbonate, and the solvent evaporated. Crystallization of the residue from mixed hexanes gave 86.1 g. (60% yield) of white prisms, m.p. 124.8–125.5°.

Anal. Calcd. for $C_{14}H_{22}O_6$: C, 58.72; H, 7.75. Found: C, 58.91; H, 7.83.

Methyl Orthoisophthalate.—Reaction of $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexachloro-$m$-xylene (Diamond Alkali Co.) with sodium methoxide in methanol as for the *para* isomer gave white plates, m.p. 95.4–96.6°, from hexane–ether.

Anal. Calcd. for $C_{14}H_{22}O_6$: C, 58.72; H, 7.75. Found: C, 58.72; H, 7.98.

α,α-Dimethoxy-α-t-butylperoxytoluene.—Methyl orthobenzoate, 18.21g. (0.10 mole) and 18.02 g. (0.20 mole) of t-butyl hydroperoxide, b.p. 21°/5 mm., n^{20}_D 1.3992, in 100 ml. of n-hexane were heated for 24 hr. in a flask equipped with an 8-in. column packed with stainless steel saddles and a total reflux-variable takeoff head. The temperature was regulated such that the pot never exceeded 70°. During this time the methanol formed during the exchange reaction was removed azeotropically and was identified by vapor phase chromatography. The remaining solvent was removed at reduced pressure and the residue distilled. In addition to recovered ortho ester and hydroperoxide, 3.45 g. of a viscous oil, b.p. 55–59°/0.09 mm. was isolated. Crystallization from pentane at −50° afforded white plates, m.p. 25.5–26.5°. An infrared spectrum indicated absorption at 1390 and 1365 cm.$^{-1}$ (t-butyl) and 862 cm.$^{-1}$ (t-butoxy). There was no absorption in the carbonyl or hydroxy regions. The peroxidic nature of the compound was indicated by the liberation of iodine from acidified sodium iodide.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.05; H, 8.51.

$\alpha,\alpha,\alpha',\alpha'$-Tetramethoxy-$\alpha,\alpha'$-di($t$-butylperoxy)-$p$-xylene.—The reaction of methyl orthoterephthalate, 16.16 g. (0.06 mole) and 36 g. (0.40 mole) of t-butyl hydroperoxide in 200 ml. of hexane was carried out as described above. Unchanged t-butyl hydroperoxide was removed at 0.1 mm. and the residue crystallized from ether–decane, 9.0 g. (37%),

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[14] M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 105 (1951).

[15] P. Gray and J. C. J. Thynne, *Nature*, **191**, 1357 (1961).

[16] This possibility was suggested by a referee.

[17] F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, and W. N. Smith, *J. Am. Chem. Soc.*, **83**, 2196 (1961).

[18] C. Walling and A. Padwa, *ibid.*, **83**, 2207 (1961).

[19] Vapor phase chromatography of gas samples were carried out on a Fisher Gas Partitioner Model 25 (Fisher Scientific Co., Pittsburgh, Pennsylvania). Liquid samples were analyzed on an Aerograph Model A-90-P (Wilkins Instrument Co., Walnut Creek, California). Infrared spectra were run on an Infracord Model 137 (Perkin-Elmer Corp., Norwalk, Connecticut). All thermometer readings are uncorrected.

[20] S. M. McElvain and J. T. Venerable, *J. Am. Chem. Soc.*, **72**, 1661 (1950).

m.p. 90.6–91.7°; an infrared spectrum indicated absorption at 845 cm.$^{-1}$ (p-substitution), 879 cm.$^{-1}$ (t-butoxy), and 1365 and 1385 cm.$^{-1}$ (t-butyl). There was no absorption in the hydroxyl or carbonyl regions. Positive peroxide test with acidified sodium iodide.

Anal. Calcd. for $C_{20}H_{34}O_8$: C, 59.68; H, 8.52. Found: C, 59.88; H, 8.16.

$\alpha,\alpha,\alpha',\alpha'$-Tetramethoxy-$\alpha,\alpha'$-di($t$-butylperoxy)-$m$-xylene.—The reaction of 5.28 g. (0.0185 mole) of methyl orthoisophthalate and 9.0 g. (0.10 mole) of t-butyl hydroperoxide in 100 ml. of n-hexane was carried out in the usual way. Solvent and excess hydroperoxide were removed under vacuum. No product distilled over at a pot temperature of 130° at 0.07 mm. The pot residue, 7.44 g. was a viscous yellow oil which resisted all efforts at crystallization. A portion, molecularly distilled at 8×10^{-4} mm. through an all glass Hickman still, gave a colorless oil at a pot temperature of 113°, n^{20}_D 1.4770, which oxidized an acidic sodium iodide solution. An infrared spectrum indicated absorption at 872 cm.$^{-1}$ (t-butoxy) and 1365 and 1390 cm.$^{-1}$ (t-butyl). A slight absorption of 1745 cm.$^{-1}$ indicated a carbonyl-containing impurity, probably dimethyl isophthalate.

Anal. Calcd. for $C_{20}H_{34}O_8$: C, 59.68; H, 8.52. Found: C, 59.92; H, 8.30.

Cumene.—Phillips Pure Grade cumene was distilled through a 30-in. column packed with stainless steel saddles, b.p. 153°. VPC indicated only a single compound.

t-Butylbenzene.—Phillips Research Grade t-butylbenzene was distilled, b.p. 169°, until it gave only a single peak on VPC.

Polymerization Initiation Activity of II.—Purified methyl methacrylate 4.727 g. (47.3 mmoles) and 0.011 g. (0.027 mmoles, 0.11 mole % peroxygen bonds) were placed in a glass ampoule and degassed by alternate freezing, evacuating, and thawing cycles. The ampoule was sealed and heated for 30 min. at 99.2°. Precipitation of the polymer from methanol gave 0.380 g. (8.0% yield) of polymethyl methacrylate, mol. wt.,[21] 2.73×10^6. In the absence of II, 0.100 g. (2.0% yield) of polymer, mol. wt., 4.24×10^6, was isolated.

Decomposition of Peroxy Ortho Esters.—The apparatus consisted of a flask of about 50-ml. capacity with a 6-in. neck to which was connected a condenser, cooled by circulating an ice–acetone mixture. The condenser was attached to a manifold bearing a 100-ml. mercury-filled buret, a mercury manometer, a two-way stopcock through which the system could be evacuated and pressured with helium, and a gas sample outlet sealed with a rubber septum. Atmospheric pressure was maintained by means of a levelling bulb attached to the buret.

The peroxide, 6 mmoles based on peroxygen bonds was dissolved in 300 mmoles of either cumene or t-butylbenzene, corresponding to 0.142 M and 0.128 M in peroxygen bonds, respectively. The system was alternately evacuated and pressured with helium until a vapor phase chromatogram of a 1-ml. gas sample indicated the absence of nitrogen and oxygen.

The reaction flask was lowered into a stirred oil bath, thermostatted at 150.0°. Zero time was taken after the first surge of gas due to expansion of the system subsided, usually about 3 min. Most of the gas was evolved during the first hour of reaction. After about 5 hr., the reaction flask was cooled to room temperature and a gas sample taken for mass spectrographic analysis.

The condenser, which was coated with paraformaldehyde, was rinsed with an acidic 2,4-dinitrophenylhydrazine solution. Crystallization of the hydrazone from ethanol gave needles, m.p. 165.5–166°, mixed m.p. with formaldehyde 2,4-DNP, 165–166°.

Gas Chromatographic Analysis.—Acetone, methanol, t-butyl alcohol, dimethyl carbonate, and benzene were determined on a 15-ft., 20% polypropylene glycol on firebrick column at 98° and a helium flow rate of 24 ml./min. Methyl benzoate was determined on a 15-ft., 7% G.E. SF-96 silicone oil on Fluoropak column at 155° and a helium flow rate of 22 ml./min. Dimethyl terephthalate, dimethyl isophthalate, and dicumyl were determined in the same silicone oil on Fluoropak column at 202° and 32 ml./min. of helium. In all cases, the total liquid reaction product and two known mixtures of about the same composition were run consecutively using the same volume of sample. Composition was determined by comparing the peak areas of the known and unknowns. The average deviation was generally less than 5%.

Infrared Analysis of Isobutylbenzene in t-Butylbenzene.—The reaction mixture from the decomposition of I in t-butylbenzene was distilled through a 36-in. spinning band column into a 1-ml. forecut, b.p. 45–167°, which contained all of the low-boiling materials as well as some t-butylbenzene solvent; a main cut, b.p. 167–171°, which was a mixture of t-butylbenzene and isobutylbenzene; and a bottom fraction which was mainly methyl benzoate containing some butylbenzenes. An infrared spectrum of the main cut indicated that it was almost pure t-butylbenzene except for a slight absorption at 737 cm.$^{-1}$. The absorbance at 737 cm.$^{-1}$ of this fraction in an 0.4-mm. cell referred to pure t-butylbenzene was compared to that of several known isobutylbenzene–t-butyl benzene mixtures. On this basis, 0.505 ± 0.003% isobutylbenzene was detected.

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