Galvinoxyl was kindly provided by Dr. G. M. Coppinger.

Benzyl iodide was prepared by the procedure of Norris,[23] and purified by the procedure of Sibbett and Noyes.[24]

Benzyl *t*-butyl ether was prepared by the method of Milas[25] except that potassium *t*-butoxide instead of sodium *t*-butoxide was used. The reaction time in excess *t*-butyl alcohol was reduced from two months at room temperature to 10 hours at 80°.

Procedure for Kinetic Runs.—A weighed sample of perester was dissolved in a known volume of the solvent, usually 25 cc. The solution was distributed into a series of sealed tubes from a manifold in an atmosphere of nitrogen. At successive time intervals, tubes were removed from the constant temperature bath and immersed in a Dry Ice–acetone-bath. The concentration at zero time was taken as that in a tube removed after about 5 minutes in the constant temperature bath. When all the samples from a kinetic run had been chilled, the percentage transmission of each one was measured at the frequency maximum of the perester carbonyl band in the infrared (5.61 μ). The procedure was essentially the same as that used by Bartlett and Hiatt.[2] The measurements were taken in a concentration range where Beer's law was obeyed as verified by a plot of log T_∞ − log T against relative concentration of perester. The kinetic equation used was

$$k_1t = \ln \frac{P_0}{P} = 2.3 \log \frac{\log T_\infty - \log T_0}{\log T_\infty - \log T}$$

In the experiments using scavengers, known solutions of scavenger and perester in the solvent were introduced separately into the two side arms of a closed apparatus sealed to a Beckman absorption cell and degassed by repeated freezing, evacuating, and warming. Finally the cell was filled with nitrogen and sealed off. After the two solutions had come to temperature in the thermostat, they were mixed at zero time, and the decrease in optical density at the selected wave length was followed in the Beckman DU Spectrophotometer. The kinetic equation used was $k = -\lambda/2(P_0)$ where λ is the slope of the plot of optical density *versus* time, P_0 is the essentially constant perester concentration and ϵ is the extinction coefficient of the scavenger.

The extinction coefficient of iodine in chlorobenzene at 510 mμ was determined as 886 ± 11. Diphenylpicrylhydrazyl and 2,4,6-triphenylphenoxy radical proved to be inefficient scavengers.

Product Analyses. The first experiment was performed in a reaction flask fitted with a side tube in which the solution of iodine in toluene could be separated from the main solution of tertiary butyl phenylperacetate in the flask. There was also a side arm provided with a great seal by which the previously sealed apparatus could be attached to another all-glass closed system. To minimize possible direct attack of iodine upon the perester, small amounts of the iodine solution were periodically introduced into the main flask by tilting the apparatus. In this way a visible iodine color was maintained in the reaction from the start. Both solutions were degassed in the usual manner to remove all oxygen or carbon dioxide. The apparatus then was sealed off under vacuum and immersed in a bath at 95 ± 3° for 7 hours, which is more than ten half lives. At the end of this time, the flask was attached to a vacuum line which then was evacuated. The break seal was broken while the reaction mixture was cooled in liquid nitrogen and the pressure of non-condensable gases was recorded. The system was re-evacuated and the reaction flask was warmed to 0°. The solvent containing tertiary butyl alcohol and ester was then distilled into the first trap of the vacuum line, cooled by Dry Ice–acetone, and the carbon dioxide was trapped by liquid nitrogen in the second trap. When all solvent had distilled over at a temperature below 0°, no pressure rise was observed in the vacuum system. The carbon dioxide trap was isolated from the system and the amount of the gas determined by pressure. The residual iodine was determined spectrophotometrically and by titration. The acetone and tertiary butyl alcohol were determined by measuring the infrared absorption at 5.79 μ and at 10.95 and 8.7 μ, respectively. The last 10 cc. of the toluene solvent removed by distillation was tested by vapor phase chromatography for the presence of ethylbenzene using a 20% silicone oil on Celite column at 90°. The fraction, however, proved to be pure toluene. The infrared spectrum of the non-volatile residue dissolved in 25 cc. of carbon tetrachloride was determined. The benzyl iodide was estimated by the sharp and characteristic band at 8.66 μ. Because benzyl iodide interferes with the bands of the second non-volatile component, benzyl tertiary butyl ether, the benzyl iodide was destroyed by heating the carbon tetrachloride solution with an excess of *n*-butylamine on the steam-bath for 5 minutes and washing the solution with hydrochloric acid, sodium carbonate and water. Traces of iodine were destroyed using a dilute bisulfite solution. Infrared analysis of benzyl tertiary butyl ether was then performed at 8.34 μ.

In the second and third product analyses the volatile products were separated by vapor phase chromatography.[13]

Acknowledgment.—We thank the National Science Foundation for support of this work, and the Deutsche Forschungsgemeinschaft for a travel grant to the junior author.

CAMBRIDGE, MASSACHUSETTS

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[23] J. F. Norris, *Am. Chem. J.*, **38**, 638 (1907).

[24] D. J. Sibbett and R. M. Noyes, THIS JOURNAL, **75**, 761 (1953).

[25] N. A. Milas, *ibid.*, **53**, 221 (1931).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

Peresters. V.[1] Di-*t*-butylperoxyoxalate

BY PAUL D. BARTLETT, ERHARD P. BENZING AND RICHARD E. PINCOCK

RECEIVED AUGUST 18, 1959

Di-*t*-butylperoxyoxalate, m.p. 50.5–51.5°, decomposes at room temperature in benzene or cumene to yield carbon dioxide (2 moles), *t*-butyl alcohol, acetone and biphenyl (7%) or bicumyl (86%). Ethers produce induced chain decomposition, which in the case of isopropyl ether is fairly rapid at 0°, and leads to isopropyl isopropenyl ether, carbon dioxide and *t*-butyl alcohol. Iodometric titration, hydrolysis and transesterification cleave the molecule with ionic scission of the perester group not initially attacked. The thermal decomposition of di-*t*-butylperoxyoxalate has ΔH^* 25.5 kcal., ΔS^* 5.1 e.u., and a calculated half-life at 60° of 6.8 minutes, placing it among the most reactive peresters previously reported. It is a low-temperature initiator for the polymerization of styrene and of diethylene glycol bis-allyl carbonate (CR 39). The mechanisms of its reactions are briefly discussed. See also Part VI.

Introduction

Previous studies in this Laboratory[1,2] have established that certain peresters undergo concerted decomposition at a C–C bond together with an O–O bond yielding carbon dioxide and an alkoxy free radical as primary decomposition products

$$RCOO{-}OC(CH_3)_3 \longrightarrow R\cdot + CO_2 + \cdot OC(CH_3)_3$$

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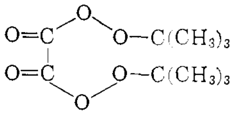
[1] (a) Part IV, P. D. Bartlett and C. Rüchardt, THIS JOURNAL, **82**, 1756 (1960); (b) presented before the Organic Division at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[2] P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958).

This decomposition mechanism, which is in contrast to that of benzoyl peroxide, shows itself most clearly in a greatly facilitated decomposition, lowered energy and entropy of activation of decomposition for those peresters in which R is capable of some stabilization as a free radical.

From the standpoint of the initiation of chain reactions this way of making rapidly decomposing compounds is self-defeating, since the most stabilized radicals, formed the most rapidly in the above reaction, are better inhibitors than initiators of chain reactions. The example of the azonitriles and other azo compounds makes it clear that a decomposition may derive driving force from the formation of a small stable molecule as well as from the formation of a stable radical. This consideration applied to the structure of peresters prompted us to try di-*t*-butylperoxyoxalate (I) which can produce no stabilized free radicals but has the possibility of yielding two molecules of carbon dioxide instead of one in a primary decomposition.



I

The investigation was undertaken to learn whether in fact this structural feature results in facilitated decomposition of this perester, what its preferred decomposition mechanism is, and what its characteristics are as a chain initiator.

Results

Preparation and Properties.—Di-*t*-butylperoxyoxalate or *t*-butylperoxalate, is mentioned only once, indirectly, in the literature.[3] It is readily prepared by dropwise addition of an anhydrous pentane solution of oxalyl chloride to a stirred solution of equivalent quantities of *t*-butyl hydroperoxide and anhydrous pyridine in the same solvent, the temperature being kept below 0°. The perester, isolated by crystallization at temperatures from −25 to −70°, is a white solid which melts at 50.5–51° on heating at the rate of 2 degrees per minute. The solid explodes readily on pounding or scratching.

Products of Decomposition.—Decomposed in benzene (5% solution) in the absence of air at 45°, *t*-butylperoxyoxalate afforded carbon dioxide in 96% of the calculated yield, together with the known products to be expected of the *t*-butoxy radical, namely, *t*-butyl alcohol and acetone, in a total yield of 90%. Small amounts of methane, ethane and biphenyl were found, and two unknown fractions representing 4.9% each of the original weight of the perester. These fractions showed intense absorption in the infrared at 5.84 μ and in the ultraviolet at 250 mμ, suggesting biphenyl derivatives; see Table I.

TABLE I

PRODUCTS OF DECOMPOSITION OF DI-*t*-BUTYLPEROXYOXALATE AT 45° (CONCENTRATION 0.25–0.5 *M*)

Compound	Amount (millimoles) In benzene	In cumene	Moles/mole perester In benzene	In cumene
Orginal perester	2.53	4,91	1.00	1.00
Methane	0.35		0.14	
Ethane	0.43		0.17	
Carbon dioxide	4.85	9.87	1.92	2.01
Acetone	1.95	0.15	0.77	0.03
t-Butyl alcohol	2.60	8.70	1.03	1.77
Biphenyl	0.17		0.07	
Bicumyl		4.20		0.86
% *t*-butyl accounted for			90	91
% CO_2 accounted for			96	100

TABLE II

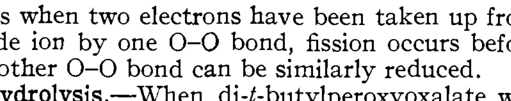
CARBON DIOXIDE YIELD FROM DI-*t*-BUTYLPEROXYOXALATE AT 45°

Solvent	CO_2, %
Benzene	96
Cumene	100
Styrene	99
Benzene + 0.7 *M* styrene	99
Isopropyl ether	100, 98, 95

Under no conditions was the yield of carbon dioxide less than 95% of the calculated maximum for complete decomposition into carbon dioxide and *t*-butoxy radical. Table II shows that in benzene, cumene, styrene and isopropyl ether the carbon dioxide yields are essentially quantitative.

The products in isopropyl ether were especially simple, consisting of 1.96 moles of carbon dioxide, 2.02 moles of *t*-butyl alcohol and 0.89 mole of isopropyl isopropenyl ether, per mole of perester. Acetone was limited to a trace.

Iodometric Titration.—The two perester groups in di-*t*-butylperoxyoxalate might potentially liberate four equivalents of iodine from potassium iodide. Actual equivalents were as follows: in aqueous acetic acid, 1.89; in 80% acetone–water with sulfuric acid, 1.95; in *t*-butyl alcohol–acetic acid, 2.02 equivalents. Evidently the attack of iodide upon one peroxy link caused immediate destruction of the other without producing any oxidation. In other experiments,[4] it was verified that any reaction leading to the ion II produces immediate ionic fission of the surviving O–O bond



$$(CH_3)_3C—O—O\underset{\|}{\overset{}{C}}\underset{\|}{\overset{}{C}}O^- \longrightarrow (CH_3)_3CO^- + 2CO_2$$

$$\quad\quad\quad\quad O\ O$$

II

Thus when two electrons have been taken up from iodide ion by one O–O bond, fission occurs before the other O–O bond can be similarly reduced.

Hydrolysis.—When di-*t*-butylperoxyoxalate was hydrolyzed in 60% acetone–water, there was always less than one peroxide group left according to subsequent iodide titration. After 3-hour standing of the perester in this solvent, only volatile products remained, and the iodine titer was 80% of two equivalents.

Basic hydrolysis was carried out with sodium hydroxide in the presence of barium chloride, and the base not precipitated was titrated to the phenolphthalein end-point. In six such hydrolyses

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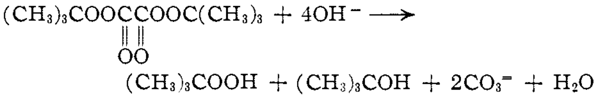
[3] W. E. Vaughan and co-workers, quoted by R. Criegee in Houben-Weyl, "Die Methoden der Organischen Chemie," 4th Ed., 1952, Vol. VIII, p. 8.

[4] See also Part VI, P. D. Bartlett and R. Pincock, THIS JOURNAL, **82**, 1769 (1960).

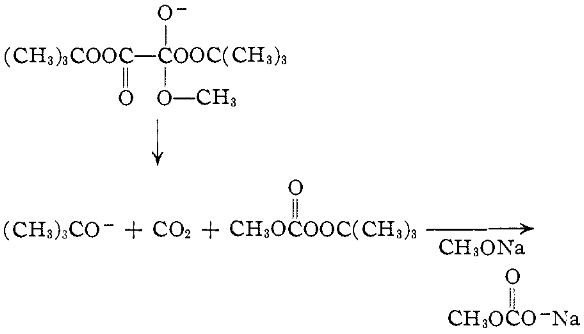
the base required was between 3.84 and 3.97 equivalents per mole of perester, and in subsequent iodometric titration 1.95–2.04 equivalents of iodine were liberated. These results indicate the equation



$$(CH_3)_3COOC(=O)C(=O)OOC(CH_3)_3 + 4OH^- \longrightarrow (CH_3)_3COOH + (CH_3)_3COH + 2CO_3^= + H_2O$$

Again the first hydrolysis sets off an ionic fission of the remaining O–O perester bond.

Even the attempt to transesterify di-*t*-butylperoxyoxalate with sodium methoxide resulted in cleavage and formation of sodium methyl carbonate. This result might possibly come from rapid induced decomposition by the solvent, or through the steps



Polymerization.—Di-*t*-butylperoxyoxalate is an efficient initiator of the polymerization of styrene and of diethylene glycol bis-allyl carbonate (CR 39), being effective at temperatures as low as 25°, and producing clear, hard products.

Rate of Decomposition.—The decomposition of di-*t*-butylperoxyoxalate was followed in benzene at 35, 45 and 55°, over a tenfold range of concentration, by observing the decline of absorption of the perester carbonyl frequency at 5.56 μ. The reactions were of the first order and, as shown by the data in Table III, the rate constants showed only slight dependence upon concentration (less than 10% increase at 35 or 45° for a tenfold change in concentration). Reaction of higher order is one evidence of chain decomposition, although the *absence* of higher-order reaction does not establish the *absence* of chain decomposition.[5,6]

From these data, by the use of the Eyring equation, ΔH^* is found to be 25.5 kcal. and ΔS^* is 5.1 cal./deg. These activation parameters and the calculated half-life at 60° of 6.8 minutes place *t*-butylperoxyoxalate in a class with such rapidly decomposing substances as *t*-butylperoxy-α-phenylisobutyrate (ΔH^* 26.1, ΔS^* 5.8)[2], which yields the cumyl free radical in the decomposition process.

Like benzoyl peroxide,[5,6] di-*t*-butylperoxyoxalate decomposes much more rapidly in an ether as solvent than in benzene. A solution 0.3 molar in *t*-butylperoxyoxalate in isopropyl ether, prepared at room temperature, erupted after about one minute as a result of the fast exothermic reaction. At 20° a 0.0347 molar solution in degassed isopropyl ether was 50% decomposed in 12 minutes, compared to a calculated half-life of 1470 minutes in benzene at this temperature. This increase in rate was eliminated by the presence of 0.2 *M* styrene,[7] which afforded a rate constant of 7.7 × 10^{-5} sec.$^{-1}$ at 35.0°. As in other cases, this result is interpretable through the view that the *t*-butoxy radical rapidly removes hydrogen from the α-position of an ether; that the α-isopropoxyisopropyl radical which results may attack either styrene (rapidly) or *t*-butylperoxyoxalate (less rapidly); and that the radicals produced from styrene, which are benzylic in character, do not attack the perester at an appreciable rate in comparison with the other possibilities open to them. Table III includes the first-order rate constants obtained; from those in the presence of styrene the enthalpy of activation is determined as 25.6 kcal., close to that in benzene.

TABLE III

RATE OF DECOMPOSITION OF DI-*t*-BUTYLPEROXYOXALATE IN SOLUTION

Solvent	Temp., °C.	Concn., mole/liter	$k \times 10^5$, sec.$^{-1}$
Benzene	35.0	0.0353	6.77
Benzene	35.0	.0797	7.02
Benzene	35.0	.328	7.44
Benzene	45.0	.0227	26.1
Benzene	45.0	.224	27.4
Benzene	55.0	.0325	93.0
Benzene	55.0	.0245	95.0
Benzene	55.0	.212	109
Isopropyl ether + 0.192 *M* styrene	35.0	.0371	7.72
Isopropyl ether + 0.201 *M* styrene	45.0	.0393	29.7
Isopropyl ether + 0.197 *M* styrene	45.0	.0292	29.8

The induced decomposition in isopropyl ether is strongly inhibited by oxygen, which produces induction periods in many cases. At room temperature and above, degassing presented a serious problem, since upon removal of oxygen the reaction became rapid and was well advanced by the time measurements could be commenced. This problem was solved by studying the rate of the induced decomposition at 0°, where it proceeded 520 times as fast as predicted by extrapolation of the first-order rate measurements on spontaneous decomposition from higher temperatures. The products of decomposition retarded the reaction, making a determination of its order difficult. The data were best fitted, however, by the equation for a 3/2 order reaction, as in the case of induced decomposition of benzoyl peroxide in many other solvents.[5]

Di-*t*-butylperoxyoxalate was also decomposed in di-*n*-butyl ether at 20°, showing induced decomposition in a lower degree and with first-order kinetics as with benzoyl peroxide in this solvent.[6]

Discussion

The activation energies of these induced decompositions were not determined.

The high rate and low activation energy of decomposition of di-*t*-butylperoxyoxalate could not be explained by any mechanism in which only an

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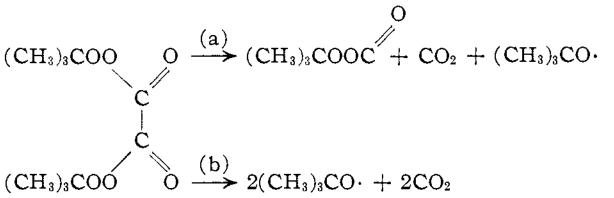
[5] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

[6] P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

[7] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

O–O bond breaks in the primary step. At least one molecule of carbon dioxide must be taking form at the transition state in order to contribute to the lowering of the activation energy from that characteristic of the unaided rupture of an O–O bond. Nothing in this paper gives a clear answer to the question whether the decomposition results from *two* bonds breaking at once, as in (a), or from concerted breaking of *three* bonds as in (b).

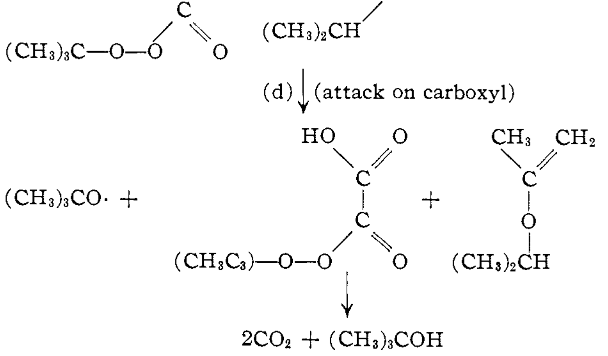


The quite clean reaction products would be consistent with (b) in any case, and would also be consistent with (a) if the carbo-*t*-butylperoxy radical is so unstable that it is unable to capture a hydrogen atom even in cumene or isopropyl ether, but always loses carbon dioxide instead. The difference between the two initial steps is that according to (a) the C–C cleavage must be as favorable energetically as the related ones previously discussed in which a cumyl or phenylallyl radical is generated; according to (b) *two* CO_2 molecules are taking form at the transition state and their incipient formation contributes energy to the over-all process. Both possibilities are *a priori* plausible. As far as (a) is concerned, the carbo-*t*-butylperoxy radical is surely not as stabilized as cumyl, but the central bond of an oxalate, between positively polarized carbon atoms, cannot be nearly as strong in the first place as the corresponding bond in an ordinary perester. Process b may seem to be opposed by an unfavorable orientational requirement, but the conformation required happens also to be more strain-free than most of the phases of rotation open to the molecule. In part VI we report some further experiments bearing upon the comparison of these two transition states.

An attempt to measure the rate of formation of radicals directly by decomposition of di-*t*-butyl peroxyoxalate in toluene at 25° in the presence of iodine resulted in a scavenger rate constant only 48% of the spectrophotometric rate constant. One is often tempted to attribute such discrepancies to the operation of solvent cage effect which permits the newly formed radicals to react with each other before they become accessible to outside reagents by diffusing apart. The present case is an interesting one, since essentially 100% of the product molecules from the *t*-butoxy radicals are formed, not by reaction of these radicals with each other, but by their capture of hydrogen atoms from the solvent itself. This capture generates benzyl radicals which are not in caged pairs, but are as free as possible to react with the scavenger. If any *t*-butoxy radical pairs were to reunite within the solvent cage, the resulting di-*t*-butyl peroxide would be found among the products, for it is stable at the temperatures of these experiments. It is clear from product studies that di-*t*-butylperoxyoxalate affords an example of a cageless decomposition mechanism, and the low counts with iodine are evidence of inefficiency of this radical scavenger. As suggested in part IV, this is probably associated with the formation of some hydrogen iodide and its reoxidation to iodine by the perester.

If di-*t*-butylperoxyoxalate is unique in undergoing cageless decomposition, it is probably because the paired *t*-butoxy radicals are separated by two carbon dioxide molecules and hence are well out of contact with each other. The decomposition of the substituted ketene imine from AIBN[8] initiates chain reactions with an efficiency which is only about 80% of that of AIBN itself. This difference is in the right direction to be due to the presence of a nitrogen molecule between the radicals in the decomposition of AIBN but not of the ketone imine. Estimates of the cage effect in *t*-butyl phenylperacetate, in which one CO_2 molecule intervenes between the radicals (part IV), place it at about 20%. It seems obvious that less cage effect is to be expected with the radicals separated by *two* molecular diameters.

Information has been scanty as to the detailed mechanism of induced decomposition of peroxidic compounds. The isolation of α-ethoxyethyl benzoate as the major product of decomposition of benzoyl peroxide in ether,[9] taken together with evidence of the chain character of the reaction, showed that the α-ethoxyethyl radical from the ether must in that case attack benzoyl peroxide with removal of a benzoate radical.[9a] In the present case no acylal has been found when *t*-butylperoxyoxalate is decomposed in isopropyl ether, but the products suggest that the chain-carrying step is donation of a hydrogen atom to the peroxyoxalate by the ether radical, producing the unsaturated ether which is found. Either of two mechanisms might accomplish this



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[8] G. S. Hammond, O. B. Trapp, R. T. Keys and D. L. Neff, THIS JOURNAL, **81**, 4878 (1959).

[9] W. E. Cass, *ibid.*, **69**, 500 (1947).

[9a] Tracer experiments have shown that attack occurs directly on a peroxide oxygen of benzoyl peroxide by an ether radical (D. B. Denney and G. Feig, THIS JOURNAL, **81**, 5322 (1959)) and even by a triphenylmethyl radical (W. von E. Doering, private communication).

The induced decomposition by transfer of β-hydrogen resembles the mechanism proposed by Swain, Schaad and Kresge[10] for decomposition of benzoyl peroxide induced by cyclohexyl radicals. Path d may be slightly preferable to (c) because of the greater ease of approach of the ether radical to an oxygen atom which is not in a position having neopentyl-like hindrance.

The reactivity of ethers toward peroxides and peresters is peculiar. They are strong hydrogen atom donors, yet the resulting ether radicals do not behave as if they possessed any special stabilization, and indeed the electronic mechanism for stabilizing an ether cation is not available for an ether radical without violating the octet rule. Ethers are probably an extreme example of the importance of polar factors in free radical reactions[11]; in the attack of an electrophilic radical on an ether molecule, the transition state can derive some energy-lowering from a polar form with an electron transferred to produce the stable ether cation at one end and the carboxylate ion at the other. Since such a structure cannot stabilize the free ether radical, it remains highly reactive, especially so in a reaction where it can displace oxygen and again produce a polar-stabilized transition state.

Experimental

Materials. *t*-Butyl Hydroperoxide.—Lucidol *t*-butyl hydroperoxide was refluxed at 30 mm. pressure in an azeotrope separation apparatus until two phases no longer separated and then distilled through a 30-cm. column under vacuum while keeping the pot temperature below 50°. After a large forerun the fraction distilling at 41° under 23 mm. pressure was collected for use. It had n^{25}D 1.3991 and was 98.2% *t*-butyl hydroperoxide by iodometric titration.

Oxalyl Chloride.—Eastman Kodak Co. oxalyl chloride was used as received.

Pyridine.—Merck reagent grade pyridine was refluxed overnight with barium oxide and distilled through a 70-cm. column packed with glass helices. The center cut boiling at 114° was stored over sodium hydroxide pellets until used.

Pentane.—Phillips technical grade pentane was stored over sodium wire before use. For the preparation of peresters the pentane used was rapidly distilled through a short Vigreux column to remove any non-volatile materials.

Benzene.—The benzene had been carefully distilled by Dr. Gideon Fraenkel and also recrystallized several times.

Cumene.—Eastman Kodak Co. white label cumene was shaken with portions of concentrated sulfuric acid until the acid layer became only light yellow on long shaking. After washing with water, sodium bicarbonate solution and water again, the cumene was dried with calcium chloride and distilled from sodium through a 90-cm. glass column packed with helices. The fraction boiling at 152–152.3° was stored in brown bottles in the dark to help prevent autoxidation.

Isopropyl and *n*-Butyl Ethers.—The ethers used were refluxed and distilled from sodium and the center fractions collected for use. The *n*-butyl ether was Eastman Kodak Co. practical grade and was distilled twice from sodium. Although no special precautions were taken to prevent contact with air during storage of the solvents, they were kept enclosed in brown bottles in the dark to help prevent the formation of peroxides. The ethers were used soon after distillation.

Di-*t*-butylperoxyoxalate.—The following procedure was found convenient for the fast preparation of this perester. A solution of 3.2 g. of oxalyl chloride in 25 ml. of anhydrous pentane was added dropwise over 20 minutes to a stirred cold solution of 4.0 g. of pyridine and 4.5 g. of *t*-butyl hydroperoxide in 50 ml. of pentane. During the addition the temperature of the solution was held between −8 and 0°. The solution was allowed to warm slowly to near room temperature and the pyridinium chloride was filtered and washed with pentane. The combined filtrate was cooled in a Dry Ice–acetone mixture and allowed to stand about 15 minutes to precipitate the perester as fine white crystals. The perester was collected quickly on a sintered glass filter, dissolved in a minimal amount of pure pentane at room temperature and the solution dried with magnesium sulfate if necessary. When this solution was cooled undisturbed at −25°, long clear crystals of perester formed. The crystals were filtered off and stored at −25°. The yield was 3.6 g. (62%) with melting point 50.5–51.5° dec. at a heating rate of 2°/min.

Near quantitative yields can be obtained by dissolving the filtered pyridinium chloride in water and filtering off the insoluble perester and by concentration of the pentane mother liquors by evaporation at low temperature. It is advisable not to scrape the crystals of perester when transferring them, especially when they are completely free of solvent.

Anal. Calcd. for $C_{10}H_{18}O_6$: C, 51.27; H, 7.74. Found: C, 51.20; H, 7.57.

Iodometric Titration.—The most convenient method for iodometric titration of peroxyoxalates was simply to dissolve a weighed amount of the perester in 10 ml. of acetic acid, add about 2 ml. of a saturated aqueous potassium iodide solution, stopper the flask and allow it to stand at room temperature for 15 to 30 minutes. The addition of a small amount of ferric chloride to the acetic acid did not seem to speed the reaction. The iodine liberated was titrated with 0.1006 *N* sodium thiosulfate solution to the disappearance of the iodine color. Blanks were run for comparison.

Using this method, for a representative titration 0.649 mmole of di-*t*-butyl peroxyoxalate would require 12.21 ml. of 0.1006 *N* thiosulfate solution or 1.89 equivalents per mole, corresponding to about one peroxide bond. Di-*t*-butylperoxyoxalate in 80% acetone–water containing potassium iodide and sulfuric acid gave 1.95 equivalents per mole. In *t*-butyl alcohol–acetic acid to which aqueous potassium iodide was added 2.02 equivalents of iodine per mole were liberated.

Di-*t*-butylperoxyoxalate in 60% Acetone–Water.—Three samples of di-*t*-butylperoxyoxalate were dissolved in 60% by volume acetone–water solutions by shaking about 10 minutes. The solutions were allowed to stand at room temperature for 3 hours. Two of the samples were treated with acetic acid and saturated potassium iodide solutions, stoppered and allowed to stand one-half and one hour, respectively, before titration with standard thiosulfate solution to the disappearance of the color of iodine. They required 1.68 and 1.65 equivalents of thiosulfate per mole of peroxyoxalate. The third sample was evaporated under vacuum at less than room temperature. No oxalic acid or any other residue was left behind. The perester had been hydrolyzed and converted to volatile products with retention of 83% of its original peroxide activity toward iodide ion.

Di-*t*-butylperoxyoxalate in Sodium Hydroxide Solution.—Samples of di-*t*-butylperoxyoxalate were added to 25 ml. of 0.0947 *N* sodium hydroxide solutions and allowed to stand for 0.5 hour at room temperature. During this time the crystals slowly dissolved; 10 ml. of 10% barium chloride solution then was added to each sample and a white precipitate of barium carbonate formed. The excess base was titrated with 0.0984 *N* hydrochloric acid solution to the phenolphthalein end-point. The results for three samples are shown in (Table IV).

TABLE IV

Sample number	I	II	III	Blank
Perester, mmole	0.4845	0.3479	0.2621	
HCl, ml.	5.16	10.22	13.63	24.18
HCl, meq.	0.508	1.006	1.341	2.379
(Meq. blank) − (meq. HCl)	1.88	1.38	1.04	
Meq. of base per mmole of perester	3.87	3.97	3.97	

To these titrated samples were added 10 ml. of acetic acid and 2 g. of solid potassium iodide. After standing 0.5 hour and warming on the steam-bath for 15 minutes the samples

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[10] C. G. Swain, L. J. Schaad and A. J. Kresge, THIS JOURNAL, **80**, 5313 (1958).

[11] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 479.

were titrated with 0.1045 *N* sodium thiosulfate solution to the starch–iodine end-point. They liberated 2.04, 1.95 and 1.97 equivalents of iodine per mole of perester.

Other samples of di-*t*-butylperoxyoxalate were hydrolyzed, the solutions acidified with sulfuric acid and analyses for oxalic acid carried out by titration with standard permanganate solution. The permanganate was decolorized only very slowly and it was shown that the *t*-butyl hydroperoxide itself would decolorize permanganate ion slowly under the same conditions. The precipitate formed on addition of barium chloride solution to hydrolyzed basic solutions of the perester was shown to be barium carbonate.

Attempted Ionic Rearrangement in Thionyl Chloride.—Di-*t*-butylperoxyoxalate, 0.0643 g., was dissolved in 10 ml. of cold thionyl chloride and the solution held at about 0° for 8 days. Evaporation under vacuum at low temperature gave a white residue identified as starting material by an infrared spectrum. The residue was dissolved in pentane and 0.348 g. (54%) of crystalline perester separated on cooling. A thorough accounting of the starting material was not carried out.

Kinetic Procedure. Spontaneous Decomposition in Benzene.—A weighed quantity of perester was transferred to a volumetric flask and dissolved in benzene. About ten aliquots of the solution were pipetted into 100 × 13 mm. Pyrex test-tubes which previously had been drawn out. The tubes were sealed at atmospheric pressure, without degassing, and placed in a wire basket. The basket was immersed in the thermostated oil-bath and shaken to bring the samples to equilibrium temperature. After about two minutes one of the tubes was withdrawn and immersed in a Dry Ice–acetone mixture. This was the zero time sample; the others were removed at suitable intervals in the same manner. The infinity sample was left in the bath for about ten half-lives. The samples were stored at −25° until infrared analysis was carried out as described below.

Induced Decompostion in Ethers.—The fast decomposition of di-*t*-butylperoxyoxalate in *n*-butyl and isopropyl ethers prevented the preparation of *degassed* solutions of this peroxyoxalate at room temperature. However, the presence of oxygen from the air dissolved in the ethers inhibited the immediate decomposition of the peroxyoxalate by an induced reaction when samples were added to the ethers at room temperature. When the oxygen was used up by reaction with ether radicals, the perester would begin to decompose much faster. A solution of di-*t*-butylperoxyoxalate in non-degassed isopropyl ether when allowed to stand at room temperature in an infrared cell would show no decrease in intensity of the carbonyl band of the perester for about 5 to 10 minutes. This induction period was followed by fast decomposition as evidenced by the beginning of movement of the spectrophotometer pen across the paper toward 100% transmission.

The method used was to dissolve a weighed amount of the perester in 25 ml. of ether at room temperature and immediately cool the solution to Dry Ice–acetone temperature. The 50-ml. round-bottom flask containing the solution was fitted with a stopper containing a nitrogen inlet tube and a tube in which to insert pipets for removing samples. These were both closed during preparation of the solution. The solution was degassed twice or three times by freezing it in liquid nitrogen, evacuating through the pipet inlet tube, allowing the solvent to warm and melt and then refreezing in liquid nitrogen. During this degassing procedure the temperature of the solution was always below Dry Ice temperature, about −70°. Prepurified nitrogen was let into the flask and the vacuum line previously connected to the pipet inlet tube was removed to allow the nitrogen to leave the flask slowly. As soon as the solvent warmed enough to redissolve the perester an "initial sample" was taken to compare with the "zero time" sample taken after the solution was equilibrated at the desired temperature.[12] The solution usually was warmed quickly to some temperature about five to ten degrees below the temperature of the run and set in the thermostated bath to complete equilibration.

Samples were taken by inserting a 1-ml. pipet into the flask, allowing the nitrogen being flushed through to remove the air from the pipet, and then pushing the pipet below the surface of the solution. The solution was pushed into the pipet by the pressure of the nitrogen. The samples were quickly cooled in a Dry Ice–acetone mixture and stored at −25° until examination on the spectrophotometer. The oxygen which entered the samples during pipetting was sufficient to prevent the induced reaction from starting again when the samples were allowed to warm to room temperature for the infrared measurements. In the case of di-*t*-butylperoxyoxalate, this inhibition allowed the measurement of the individual samples at room temperature although the samples were collected from a run at 0°.

Since the induced decomposition of di-*t*-butylperoxyoxalate at 0° did not go to completion because of inhibition by a product of the reaction and since the spontaneous decomposition was very slow at that temperature, it was necessary to remove a sample from the apparatus and decompose it at higher temperature for use as an infinity sample. Usually a sample was removed early in a run and allowed to stand in a sealed vial at room temperature or at less than 40° until complete decomposition occurred. This procedure also avoided the evaporation of solvent which would have occurred on long standing in the reaction flask under the slow stream of nitrogen. The nitrogen used in the runs at 45° was saturated with isopropyl ether at the same temperature before entering the reaction flask in order to prevent evaporation of the solvent during the run.

The temperature of the solutions was checked during the initial part of the decomposition. The decomposition of di-*t*-butylperoxyoxalate in isopropyl ether was exothermic enough to prevent the measurement of the rate at concentrations greater than about twice the minimum possible with the use of infrared methods.

In two runs with di-*t*-butylperoxyoxalate in isopropyl ether, the solvent used was obtained from a previous decomposition of the perester in degassed isopropyl ether. In both of these runs the decomposition of di-*t*-butylperoxyoxalate at 0° was inhibited completely for about 45 minutes. The preparation of the solvents was as follows:

I. Di-*t*-butyl peroxyoxalate, 0.200 g., in 25 ml. of isopropyl ether was degassed three times and allowed to warm to room temperature under nitrogen. The decomposition was completed by warming the solution under nitrogen in a water-bath at 40° for about 30 minutes; 5 ml. of pure isopropyl ether then was added. Another 0.200 g. of di-*t*-butylperoxyoxalate in 25 ml. of this decomposition solution was then used for a kinetic run at 0° following the usual procedure but taking extra care to prevent the entrance of oxygen after degassing the solution.

II. Di-*t*-butylperoxyoxalate, 0.237 g., in 30 ml. of isopropyl ether was degassed, sealed under vacuum and decomposed at 0° for 5 hours and room temperature for 16 hours further. An infrared spectrum of the resulting solution showed that complete decomposition of the perester had occurred with formation of *t*-butyl alcohol and the olefin derived from the solvent (see product studies). A further 0.210 g. of di-*t*-butylperoxyoxalate was dissolved in 25 ml. of this solvent. After degassing three times, the rate of decomposition at zero degrees was followed by the usual method. No decomposition occurred for about 45 minutes.

The induced decomposition of di-*t*-butylperoxyoxalate in isopropyl ether is stopped by the presence of 0.2 molar styrene. The runs containing styrene were carried out in glass-stoppered vials at 45°. Although the solutions were not degassed, the oxygen present was not sufficient to account for the inhibition since similar runs without styrene showed greatly increased rates.

Determination of Relative Concentration by Infrared Analysis.—The method was essentially the same as that of Bartlett and Hiatt.[2] A Perkin-Elmer model 21 infrared spectrophotometer was used with cells of 0.4 mm. thickness. After collecting all the samples of a run they were allowed to warm to room temperature and diluted, if necessary, with pure solvent to bring the concentrations within the range of about 20 to 100% transmission. The lower wave length absorption of peroxyoxalates (5.56 μ) was measured since it was farther removed from any carbonyl absorption of products of decomposition. After setting the spectrophotometer at maximum absorption on the carbonyl peak, the scanning mechanism was disconnected and the pen was set at 0 and then 100% transmission using pure solvent in both

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[12] When the "initial sample" had the same percentage transmission as the "zero time" sample then the concentration of the perester at zero time was that calculated from the amount of perester and solvent used. This check was necessary since in some runs in which the perester concentration was relatively high, considerable decomposition occurred in the time required to equilibrate the solution to the desired temperature. The actual concentration of the zero time sample is required for use of the kinetic analysis of induced chain reactions.

cells. The samples were viewed in turn against pure solvent taking care to allow time for the pen to come to equilibrium with each sample. The percentage transmission T_t could be determined within about ±0.3% in the range 20–80% where most of the samples fell.

The relative concentration at time t was calculated by the equation

$$\frac{P}{P_0} = \frac{\log T_\infty - \log T_t}{\log T_\infty - \log T_0}$$

where T_∞ is the percentage transmission of the infinity sample viewed against pure solvent and T_0 is the percentage transmission of the first sample. The use of this sort of infinity value prevented the interference in the analyses by products of decomposition which absorbed weakly in the carbonyl region. The absolute concentration, when required, was obtained by multiplying the relative concentration ratio, P/P_0, by the concentration obtained from the weight of perester and volume of solvent used. This assumed that no decomposition had occurred during the time used to bring the samples to the temperature of the run.

The validity of Beer's law was checked as follows. A solution of the perester which would give a percentage transmission of about twenty was prepared. One-half of the solution was sealed in an ampoule and heated until the perester was completely decomposed, the other half was stored at −25° to prevent decomposition. Eleven solutions with relative perester concentrations of zero to ten were made up and viewed at the low wave length carbonyl absorption band of the perester against pure solvent by the usual method. A plot of $\log T_\infty - \log T$ *versus* relative concentration was usually sufficiently straight through the range of percentage transmission used in the kinetic runs so that no correction for Beer's law deviations was needed. At higher concentrations the absorption was less than that expected by extrapolation by Beer's law from low concentration.

General Method of Product Studies.—The general technique used for analysis of the products of decomposition in various solvents was modeled after that of Bartlett and Hiatt.[3] A weighed amount of perester, usually about one gram, was dissolved in 10 ml. of solvent and the solution degassed several times by alternately freezing and melting while under vacuum. The flask then was sealed under vacuum and immersed in a constant temperature bath until perester decomposition was complete. The flask then was sealed onto the vacuum system. After evacuating the system the first trap was cooled by a Dry Ice–acetone mixture and the second by liquid nitrogen. The flask was cooled in liquid nitrogen and opened by means of a break seal to the closed, evacuated system. The pressure of the non-condensible gas was read on the manometer, a sample taken for mass spectrometric analysis, and the system again evacuated. The flask was allowed to warm to room temperature, the solvent distilled to the first trap and the gases condensible in liquid nitrogen were caught in the second trap. The condensible gas was allowed to warm to room temperature and its pressure measured. Samples of the gas were then taken for infrared and mass spectral analyses. The carbon dioxide formed was absorbed out on Ascarite and weighed. Any residual gas was analyzed by its infrared and mass spectra. From the pressure of the gases and the known volumes of the system the number of moles formed was calculated.

The solvent caught in the Dry Ice cooled trap was viewed against pure solvent in the infrared. The amount of *t*-butyl alcohol and acetone formed was found by measurement of their absorption at 2.8 and 5.84 μ, respectively, and calibrating against known solutions. The quantitative analysis of any other volatile products found in the solvent was made by infrared or gas chromatographic methods.

Isopropenyl isopropyl ether was identified without isolation by its infrared spectrum, by quantitative hydrogenation and its hydrolysis to isopropyl alcohol and acetone identified by their infrared spectra in the isopropyl ether solution.

The non-distilled residue left in the decomposition flask was chromatographed on Merck alumina and the fractions identified usually by their infrared spectra.

The accuracy of the analysis for carbon dioxide was estimated to be within about 2%. The infrared analyses were accurate to within about 5% as shown by using solutions of acetone and *t*-butyl alcohol of known concentrations to check the calibrations. The amounts of non-volatile products formed were found less accurately. The greatest effort was made to account for the compounds containing a carbonyl group.

Treatment of Experimental Data

Spontaneous Decomposition in Benzene.—Plots of $\log p/p_0$ *versus* time for decomposition of the perester in benzene were straight lines. The first-order rate constants were calculated from the slope of these lines obtained by the method of least squares using points up to 90% decomposition. The enthalpies of activation, ΔH^*, were obtained from the least squares slopes of the lines given by $\log k/T$ *versus* $1/T$ for runs at 35, 45 and 55°. The entropy of activation was calculated by substituting ΔH^* and a point on the line of $\log k/T$ *versus* $1/T$ into the equation

$$\log k/T = \log k'/h - \Delta H^*/RT + \Delta S^*/R$$

and solving for ΔS^*. (k' = Boltzmann constant, h = Planck constant.)

Induced Decomposition in Ethers. Di-*t*-butylperoxyoxalate in Isopropyl Ether.—When the decomposition of di-*t*-butylperoxyoxalate in isopropyl ether at 0° was treated as a first-order reaction, the rate constant was 520 times the value extrapolated from the measurements in benzene at higher temperatures. Since this corresponds, well within the experimental error, to pure induced decomposition, it is of no use to try by kinetic means to separate the spontaneous from the induced decomposition, as was done by Nozaki and Bartlett[5] for benzoyl peroxide decomposition in various solvents. It was also found by the same authors[6] that the induced decomposition of benzoyl peroxide in di-*n*-butyl ether shows over-all first-order kinetics, corresponding to a chain termination reaction between an α-alkoxyalkyl radical and a radical from the decomposing peroxide. Such a situation alone would invalidate any resolution into spontaneous and induced decomposition based on reaction order. The great retardation late in a run, evidently inhibition by reaction products, also makes the exact determination of reaction order difficult. The range of initial peroxyoxalate concentrations available was limited to about twofold; at concentrations below 0.03 *M* the infrared analysis was not sensitive enough, while at concentrations much above 0.06 *M* enough heat was produced by the reaction to impair the temperature control. Table V shows the results of fitting the equations for first-, 3/2- and second-order reactions to the decomposition of 0.0335 *M* and 0.0685 *M* di-*t*-butyl peroxyoxalate in isopropyl ether at 0°. These constants, determined using points up to 70% decomposition, tend to favor the 3/2 order. Thus, if auto-inhibition has been sufficiently eliminated, the chains in isopropyl ether at 0° are broken principally by reaction between two radicals from the ether.

TABLE V

COMPARISON OF CALCULATED RATE CONSTANTS AT 0° IN ISOPROPYL ETHER

Peroxyoxalate concn., *M*	Rate constants First order	3/2 order	Second order
0.0335	1.5×10^{-4}	10.4×10^{-4}	6.97×10^{-3}
0.0685	1.98×10^{-4}	9.9×10^{-4}	5.03×10^{-3}

Di-*t*-butylperoxyoxalate in *n*-Butyl Ether.—In contrast to the kinetics of decomposition of di-*t*-butylperoxyoxalate in degassed isopropyl ether, its decomposition in degassed *n*-butyl ether was more closely first order. The first-order rate constants for runs at 20° from the least squares treatment using points up to 90% decomposition were 1.59×10^{-4} sec.$^{-1}$ and 2.31×10^{-4} sec.$^{-1}$ for 0.0336 and 0.203 molar solutions, respectively.

The relatively small change in rate when the concentration of perester was increased by sixfold and the linearity of the first-order plots show the reaction to be near first order.

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