Oxygen-Rich Intermediates in the Low-Temperature Oxidation of *t*-Butyl and Cumyl Hydroperoxides

Paul D. Bartlett and Peter Günther

Contribution from Converse Memorial Laboratory of Harvard University, Cambridge, Massachusetts 02138. *Received March 26, 1966*

Abstract: The reaction of lead tetraacetate with *t*-butyl hydroperoxide at −70° produces oxygen and a product which decomposes at −30° to yield additional oxygen and to initiate chain reactions. Similar behavior is noted at the same temperatures for cumyl hydroperoxide. A scavenger of oxygen free radicals (2,4,6-tri-*t*-butylphenol), added to the solution below −30°, prevents the later oxygen evolution. α-Tetralyl hydroperoxide and 2,5-dimethyl-2,5-bishydroperoxyhexane react at −70° without producing any oxygen-rich intermediate. The conclusion is reached that the intermediate is a dialkyl trioxide, R_2O_3. Preliminary rate measurements indicate $\Delta H^* \cong 23$ kcal and $\Delta S^* \cong 20$ eu for decomposition of di-*t*-butyl trioxide. The rate constants for decomposition at −24.8° are 4.6×10^{-4} sec^{-1} for the *t*-butyl and 2.1×10^{-4} sec^{-1} for the cumyl compound.

Recent work indicates that pairs of alkylperoxy radicals, in reacting together to evolve molecular oxygen, may either terminate (1) or continue (2) the reaction chain. Reaction 2 was identified in cumene

$$2R_3COO\cdot \longrightarrow O_2{}' + R_3COOCR_3 \qquad (1)$$

$$2R_3COO\cdot \longrightarrow O_2 + 2R_3CO\cdot \qquad (2)$$

autoxidation[1,2] and shown to predominate in the decomposition of di-*t*-butyl diperoxyoxalate (DBPO) in the presence of *t*-butyl hydroperoxide.[3] The kinetics of this reaction required that termination be of second order in $R_3COO\cdot$ radicals and not in $R_3CO\cdot$ radicals, thus indicating the importance of the terminating reaction (1) under these conditions. This is not to say that direct interaction of two tertiary alkoxy radicals is impossible (reaction 3); Hiatt and Traylor[4] have recently succeeded in magnifying the cage effect in DBPO decomposition and establishing that reaction 3 must in fact have a much larger rate constant than reaction 2.

$$2R_3CO\cdot \longrightarrow R_3COOCR_3 \qquad (3)$$

k_3 for $(CH_3)_3CO\cdot$ at 35° has been variously estimated from[5] 5×10^4 to[6] 2×10^7 l./mole sec.

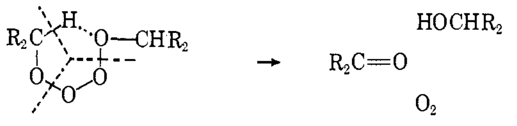
Since in the former case the rate was measured by observing an esr signal which could have been that of the *t*-butylperoxy radical as well as of *t*-butoxy, its very low value may be explicable as a misassignment.

The striking fact[7] that chain termination by interaction of α-phenylethylperoxy or tetralylperoxy radicals is about 1000 times as fast as reaction 1 finds an attractive explanation in the hypothesis[1,2,8] that a *reversible* coupling of alkylperoxy radicals (reaction 4) is much faster than reaction 1 and is but little affected by the tertiary or secondary nature of the carbon radical involved. However, when the tetroxide is secondary, it need only assume the probable conformation IIa so

$$2R_3COO\cdot \rightleftarrows \underset{\text{I}}{R_3COOOOCR_3} \qquad (4a)$$

$$2R_2CHOO\cdot \rightleftarrows \underset{\text{II}}{R_2CHOOOOCHR_2} \qquad (4b)$$

as to be rapidly destroyed by the exothermic Russell termination. This mechanism involves, accordingly,



IIa (5)

not a highly oriented collision but a favored concerted decomposition of a species (II) with a finite lifetime.

That *t*-butylperoxy radicals may combine to a labile product which can be handled at low temperatures has already been reported by Milas and Djokic[9] in the reaction of sodium *t*-butyl peroxide with ozone. The results which we now report tend to confirm these experiments, although we believe that the labile product contains three oxygen atoms, not four.[9a]

Results

***t*-Butyl hydroperoxide,** dissolved in methylene chloride and added at −70° to a solution of lead tetraacetate in the same solvent shows a vigorous oxygen evolution, while lead diacetate precipitates almost quantitatively. If the hydroperoxide is present in excess at first, further hydroperoxide additions at −70° produce no more oxygen evolution after the first evolution has ceased.

Gradual warming of the solution produces no gas evolution until the temperature reaches −30°; from there to +5° a further large volume of oxygen is

---

[1] H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).

[2] (a) P. D. Bartlett and T. G. Traylor, *ibid.*, **85**, 2407 (1963); (b) *Tetrahedron Letters*, No. 24, 30 (1960).

[3] R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, **42**, 2754 (1964).

[4] R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3766 (1965).

[5] L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, **32**, 1107 (1960).

[6] P. D. Bartlett, Reaction Mechanisms Conference, Corvallis, Ore., June 1964.

[7] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

[8] J. R. Thomas, *ibid.*, **87**, 3935 (1965).

[9] N. A. Milas and S. M. Djokic, *Chem. Ind.* (London), 405 (1962).

[9a] Note Added in Proof. Recently N. A. Milas and G. G. Arzoumanidis, *ibid.*, 67 (1966), have described a compound, stable to 80°, which they considered to be di-*t*-butyl trioxide. In this laboratory a compound prepared by their directions and having the same infrared and nmr spectra as theirs proved to be identical with the perketal, 2,2-di-*t*-butylperoxypropane, $(CH_3)_2C(OO\textit{t}\text{-}Bu)_2$ (F. H. Dickey, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **71**, 1432 (1949)). An equal mixture of the two preparation showed the same two nmr singlets at 1.22 and 1.35 ppm (internal TMS), in the ratio of 3:1, as the two materials separately. A mass spectrum showed weak peaks at mass 220 (calcd mol wt for $C_{11}H_{24}O_4$), 219, and 217, all major peaks being below 121 (unpublished work by Dr. Edward Wong: a joint publication on this subject with Professor Milas is contemplated.)

Table I. Oxygen Evolution from *t*-Butyl Hydroperoxide and Lead Tetraacetate in CH_2Cl_2

Expt no.	$Pb(OAc)_4$, mmoles	Total vol, ml (1), (2)[a]	Moles/mole of $Pb(OAc)_4$ *t*-BuOOH, (1), (2)[a]	Oxygen, $<-40°$	Oxygen $>-40°$	Moles/mole of *t*-BuOOH, total O_2	Notes
1	11.3	175	4.4	0.62	0.60	0.28	
2	22.6	175	2.2	0.44	0.17	0.28	
3	5.65	175	8.8	1.0	3.0	0.455	
4	2.8	175	17.7	1.0	5.1	0.345	
5	1.4	175	35.5	0.57	7.8	0.236	
6	11.3	175, 5	4.4, 4.4	0.44	2.8	0.37	
7	11.3	180	8.8	1.2	2.8	0.455	Extra $Pb(OAc)_4$ at end produced no further O_2
8	11.3	175, 30	4.4, 13.3	0.81	7.1	0.447	
9	11.3	190	17.6	1.5	6.6	0.457	
10	11.3	185	4.4, 13.3	0.41	7.1	0.424	~100 mmoles of *t*-BuOH added initially
11	11.3	185	4.4	0.78	0	0.177	11 mmoles of 2,4,6-tri-*t*-butylphenol added before warming
17	11.3	185	4.4	0.92	1.4	0.52	
18	5.65	100, 20	4.4, 8.8	...	6.0	...	$Pb(OAc)_2$ removed by filtration (94% yield) before warming
19	5.65	100, 20	4.4, 8.8	0.96	6.0	0.52	
20	11.3	190, 35	4.4, 13.3	0.94	7.4	0.471	Product ratio *t*-(BuOH)/(*t*-Bu_2O_2) = 20.3
21	11.3	190	4.4	0.88	1.2	0.473	Product ratio (*t*-BuOH)/(*t*-Bu_2O_2) = 7.6
22	11.3	182	1.8	0.42	0.65	0.59	Product ratio (*t*-BuOH)/(*t*-Bu_2O_2) = 5
29	11.3	190, 15	4.4, 13.2	0.79	6.81	0.43	Kinetic run, −24.8°
30	5.64	190, 15	8.8, 26.4	1.10	7.46	0.24	Kinetic run, −24.8°
31	5.64	190, 45	8.8, 35.2	1.26	9.86	0.25	Kinetic run, −33.35°
33	75	215	0.66	0.18	0.07	0.38	Hydroperoxide added all at once
34	75	265	0.66	0.20	0.08	0·.42	Hydroperoxide added gradually over 4 hr

[a] (1) is amount added originally; (2) is amount added after reaction at −70° and before warming.

emitted, its amount depending upon the excess of *t*-butyl hydroperoxide present as well as upon the original quantities of reactants. The second emission of oxygen is less than the first when lead tetraacetate is used in excess; in excess of hydroperoxide the second oxygen emission exceeds the first and may amount to 8 moles of oxygen per mole of original lead tetraacetate.

The reaction with lead tetraacetate is a well-known test for, and reaction of, hydroperoxides,[10,11] but as ordinarily carried out with *t*-butyl hydroperoxide the products are only oxygen and di-*t*-butyl peroxide. Evidently the reaction below −30° is producing a thermally unstable compound which initiates chain decomposition of the remaining *t*-butyl hydroperoxide. This would be a possible property of di-*t*-butyl tetroxide (I) whose existence as a labile intermediate we have already deduced. However, I is not the only labile compound which might be anticipated in this reaction. Indeed, because the dissociation of I yields *two* peroxy radicals, each with some spin delocalization over *two* oxygen atoms, it should be more labile than a *trioxide*[12,8]

$$R_3CO\cdot + R_3COO\cdot \rightleftarrows \underset{\text{III}}{R_3COOOCR_3} \qquad (6)$$

(III), produced in the cross-reaction (6) between an alkoxy and an alkylperoxy radical. The circumstances attending decomposition of I should be favorable for the formation of III, since the alkoxy radicals would be formed in the presence of a relatively high concentration of peroxy radicals at equilibrium with I. The trioxide should be recognizable as the *most stable* of the possible intermediates short of the stable dialkyl peroxide itself.

A cyclic analog of III is known in the initial ozonide of *trans*-di-*t*-butylethylene,[13] which can be isolated at −75°, but undergoes isomerization at −60°. This initial ozonide may be somewhat destabilized relative to an open analog by two factors: (1) the prevention of the normal skew conformation of the O_3 chain by the constraint of the five-membered ring, and (2) the assistance to its decomposition from concerted cleavage of the central C–C bond. Therefore, we might expect a compound of type III to survive to temperatures higher than −60°.

In view of the long temperature range in which no oxygen is evolved, and the conclusion reached above that the formation of I must precede any oxygen evolution from alkylperoxy radicals, it seems clear that if the intermediate in our experiments were I it should have been formed with no initial oxygen evolution at all. No conditions have been found under which the initial (low temperature) oxygen evolution does not occur. Its amount (when lead is not in excess) varies between the limits 0.41 and 1.5 moles of O_2 per mole of $Pb(OAc)_4$. The late (−30° to +5°) oxygen evolution varied in amount from 0.65 (with no excess hydroperoxide present) to 7.8 moles/mole of $Pb(OAc)_4$ (in the presence of a 35-fold excess of *t*-butyl hydroperoxide). These results are summarized in Table I.

---

(10) R. Criegee in "Methoden der organischen Chemie, Vol. 2, Houben-Weyl, Ed., Stuttgart, 1953, p 570.

(11) H. Hock and H. Kropf, *Chem. Ber.*, **91**, 1681 (1958).

(12) S. W. Benson, *J. Am. Chem. Soc.*, **86**, 3922 (1964).

(13) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

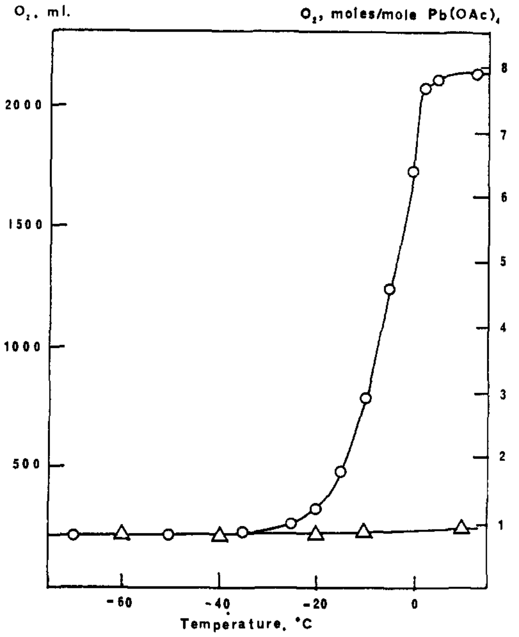


Figure 1. Oxygen evolution during slow rise in temperature following reaction at −70° between lead tetraacetate (11.3 mmoles) and t-butylhydroperoxide (4.4 mmoles) in 185 ml of methylene chloride: circles, nothing added; triangles, 2,4,6-tri-t-butylphenol (11 mmoles) added after reaction at −70°.

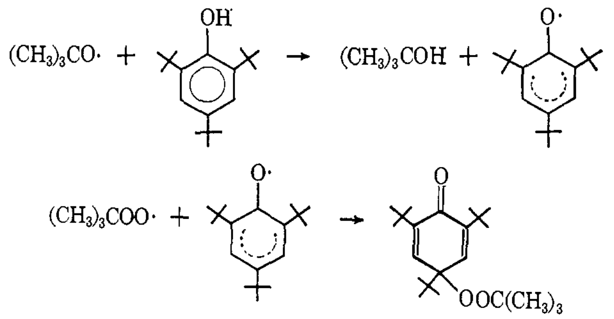
Kinetics. Preliminary kinetic studies were carried out at −24.8° in a vessel jacketed with refluxing dimethyl ether, and at −33.35° with refluxing ammonia. The rates of the secondary oxygen evolution at these temperatures were followed for 3-6 half-lives by measuring the evolved gas. The plots of log ($[O_2]_\infty - [O_2]_t$) *vs.* t were linear at −33.35°, and reasonably so after a time lag for establishment of uniform temperature at −24.8°. Table II shows the first-order rate constants observed for the di-t-butyl trioxide. These results permit a rough assignment of the activation parameters $\Delta H^* \approx 23$ kcal and $\Delta S^* \approx 20$ eu. It appears also from one rate measurement that dicumyl trioxide decomposes about half as fast at −24.8° as does di-t-butyl trioxide (see below).

Table II. Apparent First-order Rate Constants of Oxygen Evolution by Labile Intermediates in Methylene Chloride

Alkyl group	Temp, °C	k_1, sec^{-1}
t-Butyl	−24.8	4.6×10^{-4}
t-Butyl	−24.8	3.5×10^{-4}
t-Butyl	−33.35	7.2×10^{-5}
Cumyl	−24.8	2.1×10^{-4}
For t-BuOOH	$\Delta H^* \sim 23$ kcal $\Delta S^* \sim 20$ eu	

Inhibition of Secondary Oxygen Evolution. It is characteristic of the mechanism discussed above for oxygen evolution that a trioxide must first cleave into an alkoxy and an alkylperoxy radical, followed by interaction of two of the latter to produce molecular oxygen and alkoxy radicals. A good scavenger for oxygen radicals must therefore be able to prevent the secondary oxygen evolution from our intermediate. In experiment 11 of Table I, the intermediate was formed under conditions which in a control experiment (no. 17) yield 1.4 moles of secondary oxygen evolution per mole of lead tetraacetate. In experiment 11, before warming, an amount of 2,4,6-tri-t-butylphenol was added to the solution equimolar with the initial lead tetraacetate. No secondary oxygen evolution was observed on warming this solution (Figure 1). Tri-t-butylphenol is able to react in succession with two free radicals, and according to known relative reactivities[14] might be expected to show some preference for the sequence

$$(CH_3)_3COOOC(CH_3)_3 \rightarrow (CH_3)_3CO\cdot + (CH_3)_3COO\cdot$$



Reasons are given above for concluding that the intermediate is a trioxide and not a tetroxide. However, the scavenger experiment shows that in case the intermediate should be a tetroxide, its dissociation according to eq 4 must be more rapid than any concerted decomposition to evolve oxygen, since the latter process could not be inhibited by a scavenger.

Lack of Influence of Lead Diacetate. Of the methods tried for eliminating the inorganic residues after formation of the trioxide, the most successful was filtration at −70°, which led to recovery of 94% of the lead diacetate. The late oxygen evolution (6.0 moles/mole of $Pb(OAc)_4$) from this experiment (no. 18) was identical with that from a control experiment (no. 19) in which the filtration was omitted. The lead acetate is thus an inert by-product in the reaction.

Experiments with Excess Lead Tetraacetate. In two experiments (no. 33 and 34 of Table I) the absence of t-butyl hydroperoxide after low temperature reaction was assured by the use of only 50 mmoles of hydroperoxide, only one-third equivalent to the 75 mmoles of lead tetraacetate. Under these conditions, where no chain emission of oxygen from t-butyl hydroperoxide in the second stage is possible, the low- and high-temperature emissions were 0.18 and 0.07 mole per mole of initial lead tetraacetate, or 0.54 and 0.21 molecules per pair of hydroperoxide molecules (run 33). In run 34, instead of the hydroperoxide being added in a single portion, it was added gradually over a period of 4 hr, with no significant change in the amounts of the oxygen evolution in the two stages. These experiments give the most information to date about the yield of the intermediate. On the basis of $(CH_3)_3COOOC(CH_3)_3$, yielding 0.5 mole of O_2 per mole of trioxide, the yield of the trioxide was 42-48% of that theoretically possible. In the initial stage, then, (0.54 − 0.21) or 0.33 mole, 61% of the oxygen evolved, must have come from decomposition of hydroperoxide

---

(14) P. D. Bartlett and S. T. Purrington, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 20, 1964, p 2C; *J. Am. Chem. Soc.*, 88, 3303 (1966); A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

Table III. Experiments Involving Other Hydroperoxides

	Reaction at −70°			Additions after O_2 evolution,			
Expt no.	$Pb(OAc)_4$, mmoles	CH_2Cl_2, ml	ROOH, mmoles	ROOH, mmoles	O_2 (1), mmoles	O_2 (2), mmoles	Notes
14	11.3	200	Tetralyl, 48	Tetralyl, 143	6.1	0	Rapid mixing
15	11.3	200	Tetralyl, 48	Tetralyl, 143	7.7	0[a]	Slow mixing
16	11.3	185	*t*-Butyl, 49.8	Tetralyl, 47.6	10.1	11.7	*Cf.* no. 17
23	5.65	190	Cumyl, 65.8	Cumyl, 197	15	32	
24	11.3	190	*t*-Butyl, 49.8	Cumyl, 98.6	11.9	56	
32	5.65	200	Cumyl, 65.8	Cumyl, 197.4	13.2	25.3	$t_{1/2}^{-24.8°}$ = 55 min
25	11.3	200	Bis,[b] 25.3		9.1	~0	Dropwise mixing
26	11.3	200	Bis,[b] 25.3		13.4	~0	Rapid mixing
27	22.6	150	Bis,[b] 15		13.4	~0	
28	11.3	190	$(C_6H_5)_3C$, 50		3.4	0	*c*

[a] 21 g (128 mmoles) of tetralin hydroperoxide and 6.5 g of tetralone (45 mmoles) isolated after reaction. [b] 2,5-Dimethyl-2,5-bishydroperoxyhexane. [c] Dark product contained quinone and quinhydrone.

leading to peroxide instead of trioxide. The fact that this figure was not affected by the rate of addition and hence prevailing concentration of hydroperoxide is also consistent with the similar final oxygen evolutions in the pair of experiments 6 and 7, and in the pair 8 and 9 (Table I).

Product Analyses. Methods of determining the product composition at −70 to −40° are currently being investigated. In three experiments (Table I, no. 20, 21, and 22) the ratio of *t*-butyl alcohol to di-*t*-butyl peroxide in the *final* product was found by vapor chromatography to be 20.3, 7.6, and 5 when the hydroperoxide/lead ratios were 17.7, 4.4, and 1.8, respectively. These differences arose largely, at least, in the late stage where the O_2/Pb ratios were 7.4, 1.2, and 0.65. It is clear that in this range there are large effects of hydroperoxide concentration upon kinetic chain length, contrary to the situation at higher temperature, in benzene, and with DBPO as a radical source.[3]

Effect of *t*-Butyl Alcohol. In exp. 10 of Table I, 10 ml of *t*-butyl alcohol was added initially. The low-temperature oxygen evolution was cut in half, with no change in the later, high-temperature evolution. Doubling the quantity of *t*-butyl alcohol had no further effect.

Reaction of Ozone with *t*-Butyl Hydroperoxide. Ozone is known[15] to react rapidly at −25° with *t*-butyl hydroxperoxide to yield *t*-butyl alcohol, di-*t*-butyl peroxide, and acetone. Since this temperature was just above that at which the trioxide might have been stable, we reinvestigated the reaction at −45°. A solution of 1 ml of *t*-butyl hydroperoxide in 4 ml of methylene chloride acquired a blue color from accumulating ozone, which disappeared in a few minutes when the stream was interrupted. This process was repeated several times. Then on warming, the colorless solution evolved 60 ml of oxygen at −15 to +5°, suggesting a 50% yield of di-*t*-butyl trioxide.

In another experiment, in methyl chloride, the solvent was evaporated in a strong nitrogen stream at −40°. The residue was a colorless, crystalline mixture which decomposed exothermically between −15 and −5°.

Cumyl hydroperoxide behaved similarly to *t*-butyl hydroperoxide, the temperature range for secondary oxygen evolution being the same. Initial evolutions of 2.3 and 2.7 moles of O_2 per mole $Pb(OAc)_4$, and secondary evolutions of 4.5 and 5.7 moles, were observed. When *t*-butyl hydroperoxide was oxidized with lead tetraacetate at −70° and cumyl hydroxperoxide was then added, the secondary oxygen evolution was observed as with either hydroperoxide alone (Table III).

α-Tetralyl hydroperoxide showed low-temperature oxygen evolution of less than 1 mole per mole of lead tetraacetate, and *no* evolution at higher temperatures (Table III). This behavior is consistent with the mechanism, discussed above, whereby the tetralyloxy radical is never formed and so trioxide has no opportunity to be produced. The addition of α-tetralyl hydroperoxide to the low-temperature intermediate formed from *t*-butyl hydroperoxide (expt 16) cut down the secondary oxygen evolution to 1.04 moles/mole of $Pb(OAc)_4$. In a similar experiment (no. 17 of Table I) in which the addition of tetralyl hydroperoxide was omitted, the secondary oxygen evolution was 1.4 moles/mole of $Pb(OAc)_4$. In another, similar experiment (no. 6 of Table I) in which an equal increment of *t*-butyl hydroperoxide was substituted for that of tetralyl hydroperoxide, the secondary oxygen evolution was 2.8 moles/mole of $Pb(OAc)_4$.

In experiment 15 α-tetralone was isolated, although its amount (almost six times that expected from the oxygen evolution) showed that much of it may have arisen from base-catalyzed dehydration of the hydroperoxide during work-up.[16]

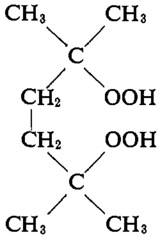
The bishydroperoxide, 2,5-dimethyl-2,5-bishydroperoxyhexane (IV), has served as a source of a cyclic peroxide (VII) by the lead tetraacetate reaction.[17] Because of the preferred intramolecular interaction of the oxygens in the expected alkanediperoxy biradical V and the related alkanedioxy radical (VI) it seemed doubtful that a trioxide would have a chance to form in this instance. As shown in Table III, experiments 25–27, the initial, low-temperature oxygen evolution was roughly equivalent to the lead tetraacetate or peroxide, whichever was the deficient component, but there was no additional oxygen evolution on warming above −70°.

---

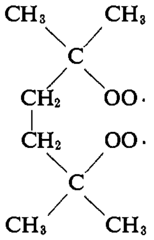
[15] D. Barnard, G. P. McSweeney, and J. F. Smith, *Tetrahedron Letters*, 14, 1 (1960).

[16] Dr. E. Rocek has found in this laboratory that this reaction interferes seriously with quantitative separations of α-tetralone and α-tetralyl hydroperoxide.

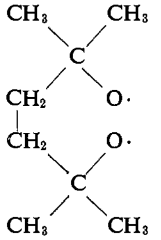
[17] R. Criegee and G. Paulig, *Chem. Ber.*, 88, 712 (1955).



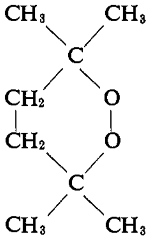
IV



V



VI



VII

Triphenylmethyl Hydroperoxide. When triphenylmethyl hydroperoxide was mixed with lead tetraacetate at −70° (exp. 28 of Table II), the immediate oxygen evolution amounted to only 30% of that to be expected from a complete conversion to bistriphenylmethyl peroxide. There was no high-temperature gas evolution, and the product was dark, containing phenolic materials and quinhydrone. Triphenylmethyl hydroperoxide is known to be subject to ionic rearrangement,[18] and here the ionic mechanism, initiated by acetic acid or by lead tetraacetate in an electrophilic role, apparently competes successfully with the oxidation mechanism.

Discussion

The Initiating Step. The most general mode of attack of an oxidizing metal ion on a hydroperoxide is the uptake of a single electron, leading to hydrogen ion and ROO· radical, or its molecular equivalent.

$$\mathrm{Pb(OAc)_4 + ROOH \longrightarrow Pb(OAc)_3 + HOAc + ROO\cdot}$$

$$\mathrm{Pb(OAc)_3 + ROOH \longrightarrow Pb(OAc)_2 + HOAc + ROO\cdot}$$

In view of the nonionic character of lead tetraacetate it is equally possible that the hydroperoxide first enters the coordination shell of the lead, either in addition to the acetate or with partial displacement of it. There is a conceivable intramolecular process leading directly to tetroxide

$$\mathrm{Pb(OAc)_2(OOR)_2 \longrightarrow Pb(OAc)_2 + RO_4R}$$

The fact that added *t*-butyl alcohol (exp. 10 of Table I) appeared to cut the initial oxygen evolution in half, while still producing the same amount of trioxide, might even be taken as an indication of a further intramolecular process capable of directly coupling *t*-butylperoxy and *t*-butoxy radicals to trioxide. In the present state of the evidence, however, the facts can be accommodated by the simple, free-radical scheme (Chart I). The effect of *t*-butyl alcohol could be a simple matter of improved solubility of the lead tetraacetate at −70°; in many of the runs this compound precipitates at the low temperature and is redissolved only during the reaction. Irregularity in the fraction of the original tetraacetate which remains dissolved is probably responsible for the fact that the initial oxygen evolutions are not as reproducible as the later ones. It does appear that, as would be expected, the oxygen evolution at −70° is highest when the excess of hydroperoxide is greatest.

The Induced Oxygen Evolution. It is now clear[3,4] that the introduction of any free radical into a solution containing *t*-butyl hydroperoxide may cause the chain evolution of oxygen from the latter with formation of di-*t*-butyl peroxide. In a nonpolar solvent the chain length (number of oxygen molecules evolved per pair of initiating radicals) is constant at about 10 at 45°, permitting the conclusion that the chain termination and oxygen evolution occur in steps of the same kinetic order in *t*-butylperoxy radicals, the termination being therefore formulated as reaction 1.[19]

The 5.5% yield of di-*t*-butyl peroxide from decomposition of DBPO at 45° in benzene,[4] interpreted[4,20] as due entirely to a cage effect, is consistent with the view that the ratio between the rates of reactions 1 and 2 is simply the ratio of the rates of cage combination and diffusion of a pair of *t*-butoxy radicals. The proposition that for *t*-butyl hydroperoxide in inert solvents (chain length = $(O_2)/(R_2O_2) = e/(1 - e)$ = (escape)/(cage reaction)) for a pair of *t*-butoxy radicals offers a simple basis for predictions which we may test by our present results.

Thomas[8] from esr measurements has concluded that ΔE_a for reactions 1 and 2 is 5.0 kcal. A combination of this with the demonstration of Hiatt[3] means that the chain length for induced oxygen evolution must fall with falling temperature, reaching $^1/_{12}$ of its 45° value at −30° and <0.01 of it at −70°. If the rate of reaction 7, which at the higher temperatures is the sole fate of the *t*-butoxy radical, should become limiting, the chain length would be reduced still further.

$$\mathrm{RO\cdot + ROOH \longrightarrow ROH + ROO\cdot} \qquad (7)$$

Unlike the induced oxygen evolution at 45°,[3] the chain length in the temperature range −33° to 0° is not independent of the hydroperoxide concentration. Figure 2 shows the oxygen yields (per mole of lead tetraacetate) plotted against the relative hydroperoxide concentrations in the second gas evolution. The highest hydroperoxide concentration represented is about 1 *M* and at this point the oxygen yield seems to be still rising. Of the steps following the initiation, the hydrogen capture by *t*-butoxy radical from ROOH is definitely the slowest and doubtless has the highest activation energy. At 45° this step is amply fast to assure that every *t*-butoxy radical which escapes the cage attacks a hydroperoxide molecule; under the conditions of our secondary oxygen evolution this must no longer be so, permitting reaction 3 (coupling of *t*-butoxy radicals) to compete with it. Cleavage of the *t*-butoxy radical would be evidenced by the presence of acetone in the product, but no product was found by vapor phase chromatography except *t*-butyl alcohol and

---

[18] H. Wieland and J. Maier, *Chem. Ber.*, **64**, 1205 (1931).

[19] Work in this laboratory (A. J. Moye and H. van Zwet, unpublished, 1961–1962) had not permitted this conclusion, for low and variable chain lengths were observed. Our work was done with DBPO in *t*-butyl hydroperoxide as solvent. This solvent brings about a lowering of the chain length for its own induced decomposition. The effect of *t*-butyl alcohol as solvent is even greater; when enough *t*-butyl alcohol is produced to make an appreciable change in the solvent during a reaction, changes in the kinetics and chain length appear (H. Stegmann, unpublished, 1964–1965).

[20] A. Factor, C. A. Russell, and T. G. Traylor, *J. Am. Chem. Soc.*, 87, 3692 (1965).

di-*t*-butyl peroxide. With regard to the chain length at −30°, we can say that the amount of initiator for the second-stage oxygen evolution cannot be greater than 1 mole per mole of lead tetraacetate, and therefore the yield of oxygen per mole of initiator (with efficient chain use of *t*-BuO·) cannot be less than 10. If this figure of 10 is being observed from less than the theoretical maximum of R_2O_3 initiator, or in spite of some diversion of *t*-butoxy radical into chain termination, then the true oxygen chain length must be correspondingly greater. It follows that a lowering of the temperature by 75° has not decreased the ratio of oxygen evolution to initiation rate at all, and has probably increased it somewhat. Cage effects which are large generally decrease slowly with rising temperature, corresponding to the competition between a coupling reaction with almost zero activation energy and a diffusion reaction conditioned by the temperature coefficient of fluidity of the solvent.[21] In the case of a very small cage effect (formerly believed to be zero) the activation energy for coupling of the radicals may so nearly match that of diffusion as to yield a cage effect either independent of temperature or even increasing slightly with rising temperature. Thus we feel that the Traylor interpretation of the competition between reactions 1 and 2 gives a good account of the low-temperature-induced oxygen evolution, and that the facts here are incompatible with any appreciable ΔE_a between reactions 1 and 2.

The considerations discussed above converge upon the following general mechanism for the oxidation of hydroperoxides.

Chart I

$$\mathrm{ROOH} \xrightarrow{\mathrm{ox}} \mathrm{ROO\cdot} \tag{i}$$

$$2\mathrm{ROO\cdot} \rightleftarrows \mathrm{ROOOOR} \tag{4a}$$

$$\mathrm{ROOOOR} \longrightarrow \underset{\text{cage}}{[\mathrm{RO\cdot\ O_2\ \cdot OR}]}$$

$$\underset{\text{cage}}{[\mathrm{RO\cdot\ O_2\ \cdot OR}]} \longrightarrow 2\mathrm{RO\cdot} + \mathrm{O_2} \tag{2}$$

$$\searrow \mathrm{ROOR} + \mathrm{O_2} \tag{1}$$

$$\mathrm{RO\cdot} + \mathrm{ROO\cdot} \underset{>-30^\circ}{\rightleftarrows} \mathrm{ROOOR} \tag{6}$$

$$\mathrm{RO\cdot} + \mathrm{ROOH} \longrightarrow \mathrm{ROH} + \mathrm{ROO\cdot} \tag{7}$$

It is evident from Table I that the chain length of induced oxygen evolution at −70° is very much smaller than at −30°. This is not due to a change in the competition just discussed between reactions 1 and 2, but chiefly to the occurrence of reaction 6, trioxide formation, which constitutes an additional mode of chain termination at −70° but not at −30°. Also if reaction 7 is significantly slow at −30° it must be still more so at −70°; the decline in rate of reaction 7 may be an important factor in making the formation of trioxide a favorable chain termination mechanism at −70°.

It is obvious that if trioxide is formed in reasonable yield in competition with peroxide at −70°, it must be capable of being formed reversibly at higher temperatures. This is in direct contradiction to a conclusion of Factor, Russell, and Traylor,[20] who showed that the *t*-butyl hydroperoxide recovered from decomposition of ^{14}C-labeled DBPO was not radioactive, and reasoned that it must have been active if reaction 6 had occurred, for the resulting labeled ROO· radical should have exchanged rapidly with ROOH. This is a serious difficulty, and we have only two suggestions concerning it. The first is that trioxide formation has a near-zero activation energy, while that of hydrogen transfer (reaction 7) may well have one of 4–10 kcal. Thus at 45° the relative rate constants of reactions 7 and 6 may have shifted in favor of the former by a factor of 36 to 8000 over the ratio at −70°. This would operate to lower the steady-state concentration of RO· and might change reaction 6 from a dominant reaction to a rare occurrence under the conditions of ref 20.

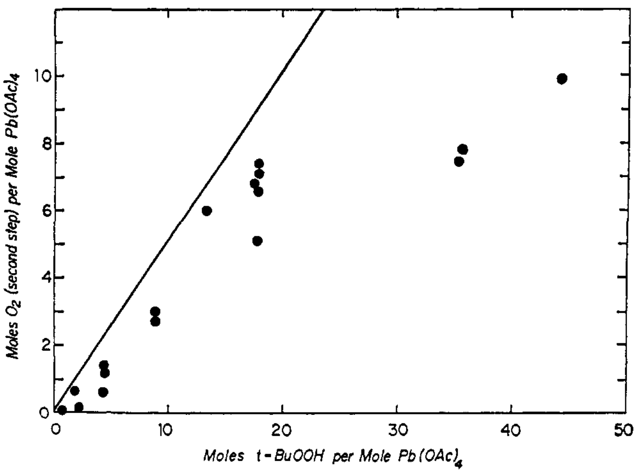


Figure 2. Dependence of second-stage oxygen evolution (above −30°) on *t*-butylhydroperoxide/lead tetraacetate ratio. The solid line represents the maximum oxygen evolution for complete conversion of the *t*-BuOOH present to $t\text{-Bu}_2O_2 + O_2$.

The second suggestion is one that has already been made by Thomas and Tolman,[22] to which we add a relevant experimental observation. These authors, seeking an explanation for the lack of a kinetic isotope effect in the reaction of cumyl hydroperoxide with TOOD (T = α-tetralyl), considered the possibility that the observed interaction was not by capturing the hydroxylic hydrogen, but the α hydrogen. It was observed by Traylor[23] in this laboratory that azo-α-phenylethane is autoxidized with a kinetic chain length over 10^4, the reaction involving attack of an oxygen radical upon the α hydrogen, and Swigert has observed that the susceptibilities of azo-α-tetralin and tetralin toward α attack by oxygen radicals were in the ratio of about 8:1.[24] There is thus analogy for a high reactivity of the kind in tetralins substituted by electron-rich atoms. This second suggestion could be an "explanation" of the Factor, Russell, and Traylor[20] results only in the sense that it would obviate the necessity of believing in a very rapid symmetrical transfer of hydrogen between *t*-butylperoxy radical and *t*-butyl hydroperoxide.

Experimental Section

t-Butyl hydroperoxide was obtained from the Lucidol Co. and purified by fractional distillation. Cumyl hydroperoxide was a commercial sample purified by fractional distillation. 2,5-Di-

---

(21) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 145 (1966).

(22) J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2079 (1962).

(23) P. D. Bartlett and T. G. Traylor, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March 21–29, 1962, p 34-O.

(24) Recalculated from R. D. Swigert, Thesis, Harvard University, 1964, p A-III-2.

methyl-2,5-bishydroperoxyhexane was purchased from Lucidol under the trade name Luperox-2,5-2,5. It was washed several times with ice water, dried, and recrystallized from benzene, mp 104°. Its purity by iodometric titration was 98.5%.

The reactions at −70° were carried out in a Dry Ice–acetone bath in a 250-ml flask from which the effluent gas was conducted to a graduated cyclinder and collected by displacement of water. The reaction mixture was stirred magnetically, and the temperature was read periodically with a low-temperature thermometer. One hour was ordinarily allowed for completion of the low-temperature gas evolution, after which no further oxygen appeared until the temperature was raised by more than 35°.

In expt 3 the gas produced was analyzed mass spectrometrically. It consisted entirely of oxygen except for some nitrogen, which was expected because no precautions were taken to exclude air.

In expt 18 a special apparatus was constructed in which the bottom of the reaction vessel contained a fritted glass filter. The reactants were held in the reaction flask by a positive pressure of nitrogen introduced below the fritted glass. After completion of the reaction at −75°, the nitrogen pressure was released, and the solution filtered into a lower vessel, the entire assembly being surrounded by the cooling bath. The upper vessel was then removed, and a precooled solution of 5 ml of *t*-butyl hydroperoxide in 15 ml of methylene chloride was added to the clear filtrate in the lower flask which was magnetically stirred and connected to a gasometer. After this addition was completed without gas evolution, the reaction mixture was warmed up, and the oxygen measured as reported in Table I.

The product analyses were performed by vapor phase chromatography on a 6-ft diisodecyl phthalate column between 45 and 75° without heating the injection port or detector block.

Acknowledgment. This work was supported by the B. F. Goodrich Co.

Peresters. XII. *t*-Butyl Triphenylperacetate

John P. Lorand and Paul D. Bartlett

Contribution from the Converse Memorial Laboratory, Harvard University,
Cambridge, Massachusetts 02138. *Received March 26, 1966*

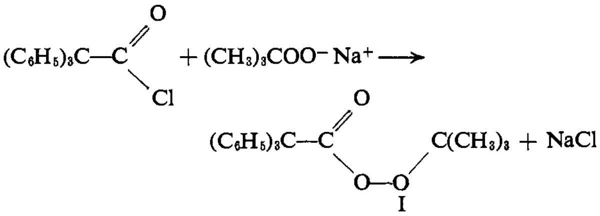
Abstract: The reactive perester, *t*-butyl triphenylperacetate, decomposes in cumene at 25° with $k = 1.7 \times 10^{-4}$ sec^{-1} (more than 40 times faster than the diphenylperacetate), $\Delta H^* = 24.1$ kcal, $\Delta S^* = 4.9$ eu. The yield of carbon dioxide is 95–98% and the solution shows the esr spectrum of the triphenylmethyl radical. There is a cage effect of about 10%; the coupling product of the triphenylmethyl and *t*-butoxy radicals is mono-*p*-*t*-butoxytriphenylmethane (IV); spectral evidence indicates a similar amount of triphenylmethyl *t*-butyl ether (II) in the early product, which is converted during chromatography to triphenylcarbinol. The principal product in styrene is a "one-unit telomer" (VI) produced by addition of *t*-butoxy radical to the primary end of the styrene molecule, followed by coupling of the resulting radical with triphenylmethyl. Although this reaction involves a coupling of the triphenylmethyl radical at its central carbon atom, attempts to synthesize the normal ether II from halide and alkoxide, or the telomer chain of VI from phenylmalonic ester and triphenylmethyl chloride, afforded only further examples of attack at the *para* position of the triphenylmethyl halide.

That the decomposition of numerous *t*-butyl peresters proceeds by concerted two-bond cleavage into a pair of free radicals and a molecule of carbon dioxide has been well documented.[1] The rate of decomposition of a perester $RCO_3C(CH_3)_3$ depends in part on the stability of the radical R·. The ultimate products of decomposition result from reactions of the radicals R· and *t*-butoxy.

Although peresters of most of the simple phenyl- and methyl-substituted acetic acids had been studied, that of triphenylacetic acid had eluded preparation.[2] We now report its preparation and reactions. Although its rate of decomposition is in accord with expectation, its products are atypical, including an example of the ambident reactivity of triphenylmethyl radical. Proofs of structure of two products of decomposition have led to new examples of the ambident reactivity of triphenylchloromethane.

Results

Preparation and Purification of the Perester. Apparently because of the extreme bulk of the triphenylmethyl group, triphenylacetyl chloride had previously been found to be unreactive with *t*-butyl hydroperoxide and pyridine. However, the use of the sodium salt of the hydroperoxide led, in up to 55% yield, to crystalline perester I, mp 61–64° (effervescence), λ_{max} 5.67 μ; I, recrystallized from benzene–pentane at −20°, could be stored at that temperature for 8 months unchanged.



$$(C_6H_5)_3C{-}C(=O)Cl + (CH_3)_3COO^-Na^+ \longrightarrow (C_6H_5)_3C{-}C(=O){-}O{-}O{-}C(CH_3)_3 + NaCl \quad (1)$$

I

Satisfactory elementary analyses were obtained, but iodometric titration by the method of Silbert and Swern[3a] gave an apparent purity of only 73%. Such a result is characteristic of the less stable peresters.[3b] A more positive criterion of purity is the nearly quantitative yield of carbon dioxide from thermal decomposition of the perester in all the solvents used in this study (see below).

---

[1] (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); (b) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960); (c) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963); (d) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960).

[2] P. D. Bartlett, *Experientia Suppl.*, **7**, 275, 282 (1957).

[3] (a) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); (b) J. P. Lorand, Thesis, Harvard University, 1964, p 8.