Acetaldehyde Autoxidation. I. Products of Termination[1]

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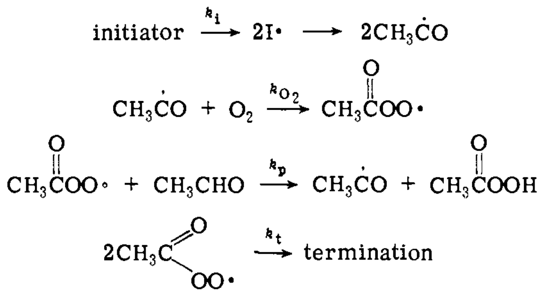
Abstract: The products of the termination process associated with free radical induced autoxidation of acetaldehyde have been determined. Because carbon dioxide is one of these products, and acetyl peroxide is absent, a decomposition of acetyl tetroxide directly to methyl radicals, carbon dioxide, and oxygen is proposed.

The initiated autoxidation of aldehydes obeys the kinetic equation

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_p(\text{aldehyde})(\text{initiator})^{1/2}(k_i/2kt)^{1/2} \quad (1)$$

at oxygen pressures above about 200 Torr.[2,3] This result, structural dependence upon rate, detailed kinetic studies, etc. strongly support the chain mechanisms shown in eq 2-5. Initiation (2)[4] and propagation steps (3,4)[2,3] are well understood, but the termination process (5) is not.[3]



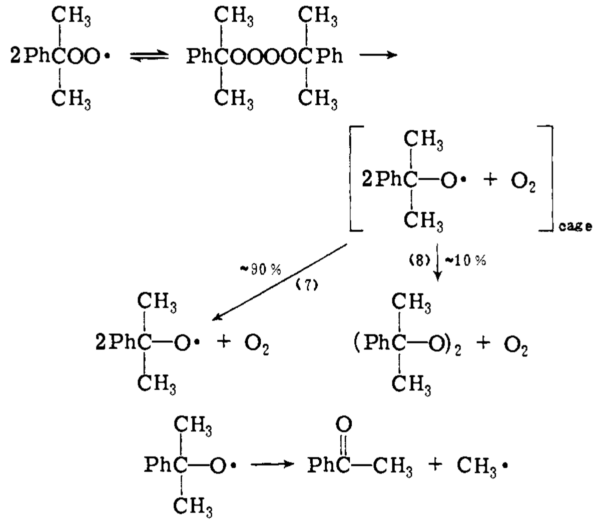
$$\text{initiator} \xrightarrow{k_i} 2\mathrm{I}\cdot \longrightarrow 2\mathrm{CH_3\dot{C}O} \quad (2)$$

$$\mathrm{CH_3\dot{C}O} + \mathrm{O_2} \xrightarrow{k_{O_2}} \mathrm{CH_3\overset{O}{\overset{\|}{C}}OO\cdot} \quad (3)$$

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}OO\cdot} + \mathrm{CH_3CHO} \xrightarrow{k_p} \mathrm{CH_3\dot{C}O} + \mathrm{CH_3\overset{O}{\overset{\|}{C}}OOH} \quad (4)$$

$$2\mathrm{CH_3C}\!\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OO\cdot}\end{smallmatrix} \xrightarrow{k_t} \text{termination} \quad (5)$$

Termination processes[2,4] for tertiary[5-8] and secondary[9,10] hydrocarbon autoxidations have been studied in detail using isotopic labeling[6a,b] and other techniques. Termination of tertiary peroxy radicals has been shown to proceed through a tetroxide to a caged alkoxy radical pair and subsequently to result in termination through methylperoxy radicals which are produced by splitting the oxy radicals (eq 6-11).[5,6,11] Because, at ordinary viscosities of 5-10 mP, reaction 7 is about ten times as fast as reaction 8, the termination of tertiary peroxy radicals proceeds mostly through the very rapid reaction 11.[12-14] This cyclic process is rather well documented for other peroxy radicals of the type $(\mathrm{R_2CHOO\cdot})$.[9,15]



$$2\mathrm{Ph}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{OO\cdot} \rightleftharpoons \mathrm{Ph}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{OOOO}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{Ph} \longrightarrow \left[2\mathrm{Ph}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}O\cdot} + \mathrm{O_2}\right]_{\text{cage}} \quad (6)$$

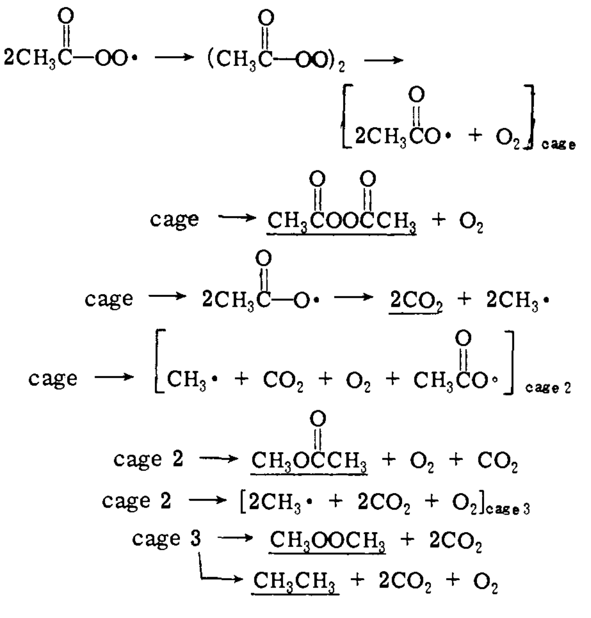
$$\xrightarrow[(7)]{\sim 90\,\%} 2\mathrm{Ph}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}O\cdot} + \mathrm{O_2} \qquad \xrightarrow[(8)]{\sim 10\,\%} (\mathrm{Ph}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}O})_2 + \mathrm{O_2}$$

$$\mathrm{Ph}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}O\cdot} \longrightarrow \mathrm{Ph\overset{O}{\overset{\|}{C}}{-}CH_3} + \mathrm{CH_3\cdot} \quad (9)$$

$$\mathrm{CH_3\cdot} + \mathrm{O_2} \longrightarrow \mathrm{CH_3OO\cdot} \quad (10)$$

$$\mathrm{CH_3OO\cdot} + \cdot\mathrm{OOR} \longrightarrow \mathrm{CH_2O} + \mathrm{O_2} + \mathrm{ROH} \quad (11)$$

A similar, but more complex, process could be envisioned for acetylperoxy radicals in which the acetoxy radical would be more prone to cleave than was the cumyloxy radical (eq 12-19).[16] Beside these five possible cage products, there are three termination products which could result from the rapid reactions of the methyl or methylperoxy radicals which escape the cage (eq 20 and 21). The problem is further complicated by the possible cyclic process proposed by McDowell and Sifniades (eq 22).[4,17]



$$2\mathrm{CH_3\overset{O}{\overset{\|}{C}}{-}OO\cdot} \longrightarrow (\mathrm{CH_3\overset{O}{\overset{\|}{C}}{-}OO})_2 \longrightarrow \left[2\mathrm{CH_3\overset{O}{\overset{\|}{C}}O\cdot} + \mathrm{O_2}\right]_{\text{cage}} \quad (12)$$

$$\text{cage} \longrightarrow \underline{\mathrm{CH_3\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}CH_3}} + \mathrm{O_2} \quad (13)$$

$$\text{cage} \longrightarrow 2\mathrm{CH_3\overset{O}{\overset{\|}{C}}{-}O\cdot} \longrightarrow \underline{2\mathrm{CO_2}} + 2\mathrm{CH_3\cdot} \quad (14)$$

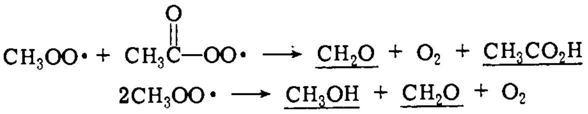
$$\text{cage} \longrightarrow \left[\mathrm{CH_3\cdot} + \mathrm{CO_2} + \mathrm{O_2} + \mathrm{CH_3\overset{O}{\overset{\|}{C}}O\cdot}\right]_{\text{cage 2}} \quad (15)$$

$$\text{cage 2} \longrightarrow \underline{\mathrm{CH_3O\overset{O}{\overset{\|}{C}}CH_3}} + \mathrm{O_2} + \mathrm{CO_2} \quad (16)$$

$$\text{cage 2} \longrightarrow [2\mathrm{CH_3\cdot} + 2\mathrm{CO_2} + \mathrm{O_2}]_{\text{cage 3}} \quad (17)$$

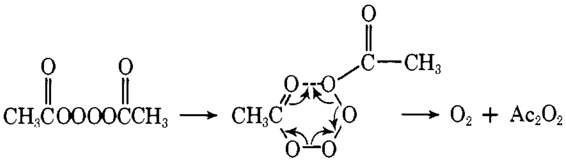
$$\text{cage 3} \longrightarrow \underline{\mathrm{CH_3OOCH_3}} + 2\mathrm{CO_2} \quad (18)$$

$$\phantom{\text{cage 3}} \hookrightarrow \underline{\mathrm{CH_3CH_3}} + 2\mathrm{CO_2} + \mathrm{O_2} \quad (19)$$



$$\mathrm{CH_3OO\cdot} + \mathrm{CH_3\overset{O}{\overset{\|}{C}}{-}OO\cdot} \longrightarrow \underline{\mathrm{CH_2O}} + \mathrm{O_2} + \underline{\mathrm{CH_3CO_2H}} \quad (20)$$

$$2\mathrm{CH_3OO\cdot} \longrightarrow \underline{\mathrm{CH_3OH}} + \underline{\mathrm{CH_2O}} + \mathrm{O_2} \quad (21)$$



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}OOOO\overset{O}{\overset{\|}{C}}CH_3} \longrightarrow \cdots \longrightarrow \mathrm{O_2} + \mathrm{Ac_2O_2} \quad (22)$$

Although the possibilities are many, the number of possible gaseous termination products and the variety of $^{18}\mathrm{O}$-labeling possibilities make the experimental investigation of

Table I. Oxygen Uptake ($-d[O_2]/dt$) and Chain Length (L) for Aldehyde Autoxidations in Benzene, with and without Added DBPO

RCHO	Temp, °C	[RCHO], M	[DBPO], $M \times 10^3$	$-d[O_2]/dt$, M sec^{-1} × 10^5 [a,b]	L
CH_3CHO	25	0.32	0	0[c]	0
			2.78	2.53[d]	371
C_2H_5CHO	25	0.26	0	0[c]	0
			2.78	6.71	985
i-C_3H_7CHO	25	0.20	0	0[c]	0
			2.78	8.01	1174
$C_6H_{11}CHO$	25	0.13	0	0[c]	0
			6.51	5.79	369
t-C_4H_9CHO	10	0.17	0	0.137	
			6.84	0.89	47

[a] Amounts of gas absorbed corrected to M in solution. [b] Volume of solution 19.78 ml, gas volume 69.71 ml, constant volume runs. [c] Less than 10^{-3} M of O_2 absorbed in interval of 1000 sec. [d] Predicted rate is about 2×10^{-4} M sec^{-1} using the published k_p, k_t, k_i, and initiator efficiency. See text.

aldehydes somewhat more definitive than those of hydrocarbons. There are more easily available mechanistic "handles" than there were in cumene autoxidation.

Results

Our first objective was therefore a semiquantitative determination of just which products are actually produced in acetaldehyde termination in the liquid phase.

In order to do this, we must first show that our initiated system is well-behaved kinetically and, for convenience and kinetic simplicity, we must devise some way of maintaining constant rate of oxygen consumption as was done in cumene autoxidation.[6] To accomplish this end with the very reactive aldehydes[2,18] and have manageable rates and chain lengths, low concentrations of aldehyde and high initiation rates are necessary. These were achieved by first determining the oxidation rate for about 0.3 M aldehyde concentration and then adding aliquots of aldehyde at intervals so as to maintain approximately constant 0.3 M aldehyde concentration. In this way, constant oxidation rates were obtained. We report kinetic behavior of several aldehydes.

Absence of Self-Initiation. Aldehydes were dissolved in purified benzene and exposed to 1 atm of oxygen at 25° and the oxygen uptake measured by following the pressure change. After about 1000 sec, a concentrated benzene solution of di-*tert*-butylperoxy oxalate was added. It can be seen in Figure 1 for propionaldehyde that oxidation was quite negligible until initiator was added.

Table I shows the results of similar autoxidations of other aldehydes. In all cases except pivaldehyde, autoinitiation was negligible under our conditions. The rate of initiated acetaldehyde autoxidation is, on the other hand, in good agreement with that predicted from the known rate constants, $k_p = 3 \times 10^3$ M^{-1} sec^{-1},[3] $k_t = 5 \times 10^7$ M^{-1} sec^{-1},[3] and $k_i = 1.41 \times 10^{-5}$ sec^{-1},[19] and initiator efficiency, $e = 0.87$[13] in benzene at 25°.

Conversion to Peracids. In order to determine that peracids were actually the products produced by the consumed oxygen, the solutions were analyzed for peroxide function simultaneously with oxygen uptake measurements. Plots of both oxygen uptake and "active oxygen" are shown in Figures 2, 3 and 4.

It is clear that acetaldehyde is oxidized cleanly to the peracid until a concentration of about 0.5 M is obtained. At this point, the Baeyer-Villiger reaction probably becomes important (eq 23). Although this reaction becomes important and interferes with the maintenance of accurate kinetic parameters at about 0.2 M for other aldehydes, it does not alter the kinetics of our acetaldehyde reactions under the conditions studied. At any rate, the result of reaction 23 is the uptake of two aldehydes for each oxygen instead of one for one if reaction 23 were negligible. There is no problem with acetaldehyde until 10^4 sec (under our conditions).

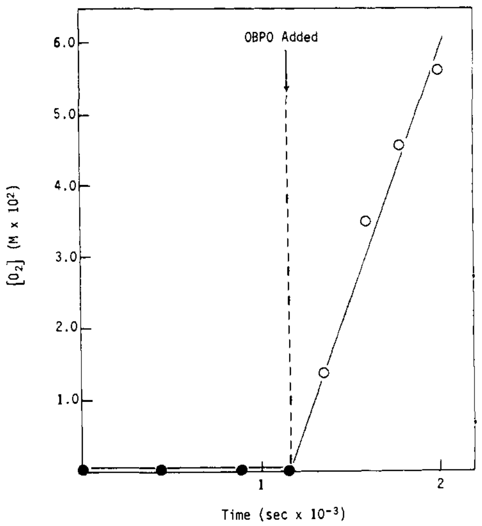


Figure 1. Concentrations of oxygen ($[O_2]$) absorbed vs. time for autoxidation of C_2H_5CHO in benzene. ●, [DBPO] = 0 (slope $<10^{-6}$ M sec^{-1}); ○, [DBPO] = 2.8×10^{-3} M (slope = 6.71×10^{-5} M sec^{-1}).

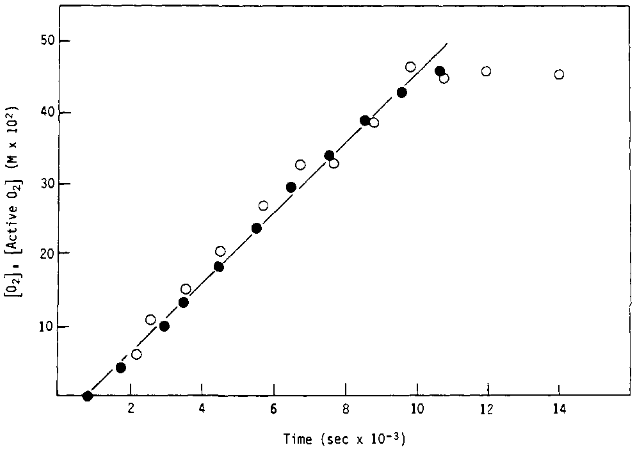
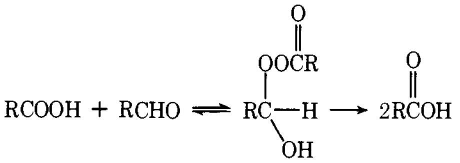


Figure 2. Concentrations of oxygen ($[O_2]$) absorbed and concentrations of "active oxygen" ([active O_2]) vs. time for autoxidation of CH_3CHO; ●, $[O_2]$; ○, [active O_2]. 0.2130 ml of aldehyde are added every 1000 sec to maintain ~0.3 M aldehyde concentration.



$$RCOOH + RCHO \rightleftharpoons RC(OOC(=O)R)(OH)H \longrightarrow 2RC(=O)OH \qquad (23)$$

Products of Termination. In a typical product determination, conditions shown in Table I were maintained for about 10^4 sec, the solution was quenched at −20°, and the autoxidation was stopped by adding a small amount of 2,6-di-*tert*-butyl-*p*-cresol. Except for CO_2, which was determined periodically, all products were determined at a single point (~10^4 sec) by various gas-liquid phase chromatographic procedures described in the Experimental Section.

Using internal standards and control oxidations to assure that all of the possible termination products survive the autoxidation conditions, we obtained the results shown in

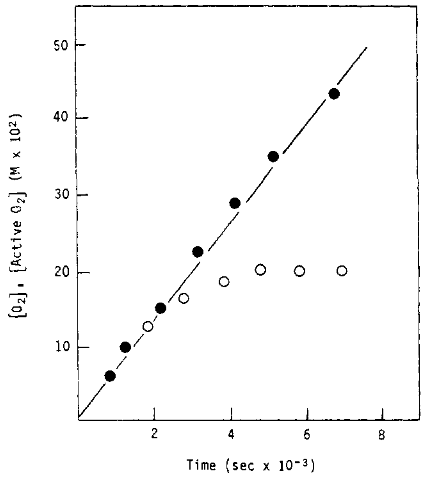


Figure 3. Concentrations of oxygen ($[(O_2]$) absorbed and concentrations of "active oxygen" ([active O_2]) vs. time for autoxidation of i-L_3H_7CHO: ●, $[O_2]$; ○, [active O_2].

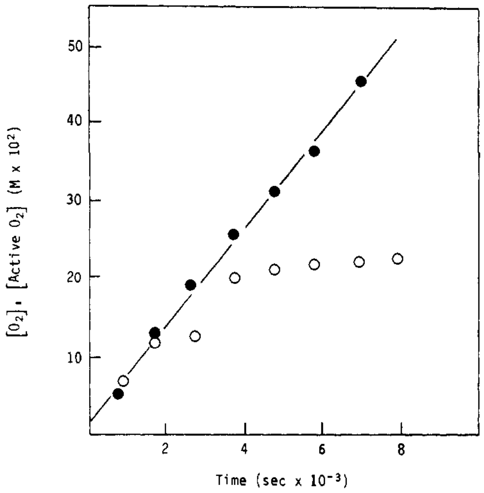


Figure 4. Concentrations of oxygen ($[O_2]$) absorbed and concentrations of "active oxygen" ([active O_2]) vs. time for autoxidation of C_2H_5CHO: ●, $[O_2]$; ○, [active O_2].

Table II. In this table, the yields are quoted in terms of percentage of that demanded by 100% termination through the mechanism producing that product.

The striking thing about this table is that, except for CO_2, *none* of the proposed cage products—ethane, acetyl peroxide, methyl acetate, or methyl peroxide—is produced in any appreciable fraction of calculated termination yields. The apparent exception, methyl acetate, was shown to be an artifact resulting from esterification of methyl alcohol by the product acetic acid. When chloroacetic anhydride was present during the autoxidation to trap methanol, the methyl acetate became undetectable. We set a maximum of 7% on its possible concentration, because the determination of trace amounts of methyl acetate in benzene solutions of products has some experimental difficulties.

It was important to establish the presence or absence of acetyl peroxide, because it had been reported as a product of gas-phase acetaldehyde autoxidation.[17] Rather than risk a direct analysis for this unstable peroxide, we chose to take advantage of a cage reaction which has been repeatedly confirmed for this compound (eq 24).[20-22] If induced decomposition is prevented, ethane production necessarily results from the peroxide bond scission if acetyl peroxide is present. Therefore, after autoxidizing acetaldehyde for 4 × 10^4 sec, the autoxidation mixture was made 0.5 M in 2,6-di-*tert*-butyl-*p*-cresol to stop autoxidation[3] and heated to 80° for 5 hr to decompose the acetyl peroxide. The gas phase was then analyzed for ethane. Although only a small trace of ethane was detected (by the very sensitive FID detector) in the ordinary autoxidation, the predicted amount of ethane was produced when an amount of acetyl peroxide commensurate with termination was added to the solution before starting the autoxidation.

Table II. Products from CH_3CHO Autoxidation

Product	% Product[a]	Analysis system[b]
C_2H_6	$<10^{-3}$	2
CO	$<10^{-3}$	2
CO_2	400	1, 2
$CH_3\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}CH_3$	<6[c]	2
$CH_3O\overset{O}{\overset{\|}{C}}CH_3$	<7[d,e]	3
$CH_3O\overset{O}{\overset{\|}{C}}CH_3$	17.5[f]	5
CH_3OH	10.8[g]	5
CH_3OH	28.3[h]	5
CH_3OOCH_3	<6[e]	4

[a] % product = (moles of product/moles of termination interactions expected) × 100. [b] See Experimental Section. [c] Based on yield of C_2H_6 from decomposition of added $(CH_3C(=O)O)_2$. [d] With added chloroacetic anhydride. [e] Based on instrumental limits of detectability, never actually detected. [f] Maximum amount observed, in absence of added chloroacetic anhydride. [g] Observed amount. [h] Observed amount plus observed amount of $CH_3OC(=O)CH_3$.

$$(CH_3\overset{O}{\overset{\|}{C}}O)_2 \xrightarrow[\text{traps}]{\text{radical}} [11\%\ \text{ethane}]_{\text{cage}} + [24\%\ CH_3\overset{O}{\overset{\|}{C}}OCH_3]_{\text{cage}} \qquad (24)$$

Products of Methyl Radical Oxidation. The products of reaction of methyl radicals with oxygen are difficult to determine in the presence of peracetic acid. We therefore analyzed for such products in the absence of aldehyde by simply allowing DBPO to decompose in an atmosphere of oxygen in benzene. Under these conditions, 37% of the *tert*-butoxy radicals cleave to give methyl radicals.[19] The products derived from oxidation of these radicals are listed in Table III.

It is clear from this table that methyl radicals are oxidized to formaldehyde and possibly formic acid as well as, presumably, methyl hydroperoxide as required by methylperoxy radical termination. The absence of methanol in this determination is unexpected. In a separate experiment in which acetyl peroxide was decomposed in an oxygen atmosphere, methanol was observed. Both methanol and formaldehyde have been reported as products of gas-phase oxidation of methyl radicals.[23] The methanol was possibly oxidized to formaldehyde or formic acid during the DBPO decomposition. At any rate, methanol is a product of acetaldehyde autoxidation, and it very probably comes from methylperoxy radical termination.

Of the possible termination products, we have found only CO_2, methanol, and possibly methyl hydroperoxide. Although formaldehyde was not analyzed directly in the acetaldehyde autoxidation, we did observe the production of acetaldehyde during propionaldehyde autoxidation, and acetone plus 2-propanol were observed as products of isobutyraldehyde autoxidation.

Discussion

The cyclic reaction (22) or any other cyclic process giving termination would produce 1 mol of acetyl peroxide and

Table III. Products of Decomposition of Di-*tert*-butyl Peroxyoxalate at 25° in the Presence of Oxygen

Product	Yield, moles/mole Me·	Yield, moles/mole DBPO	Experimental conditions	Analytical method
CO_2		1.9–2.0	0.25 *M* in benzene[a]	
CO	0.054	0.04	0.139 *M* in chlorobenzene	GLC
H_2O		<0.01	0.441 *M* in benzene	Karl Fischer,[b] GLC
CH_3OH		~0	0.139 *M* in chlorobenzene	GLC
t-BuOH		0.856	0.139 *M* in chlorobenzene	GLC
Acetone	(1)	0.738	0.139 *M* in chlorobenzene	GLC
t-BuOO-*t*-Bu		0.13[c]	0.139 *M* in benzene	GLC
CH_4		~0	0.143 *M* in chlorobenzene	GLC
C_2H_6		~0	0.143 *M* in chlorobenzene	GLC
CH_3OCH_3		~0	0.143 *M* in chlorobenzene	GLC
CH_2O	0.216	0.16	0.441 *M* in benzene	Tollens reagent[b]
"HCOOH"	0.51	0.376	0.441 *M* in benzene	Titration[d]
"CH_3OOH"	0.14	0.10	0.162 *M* in benzene	KI titration
Total Me· product	0.92			

[a] Data of Bartlett, Benzing, and Pincock, *J. Am. Chem. Soc.*, 82, 1763 (1960). [b] Hydroperoxide was shown not to interfere with Tollens reagent titration or with Karl Fischer titration. [c] Data of Hiatt and Traylor, ref 13. [d] Total acid after CO_2 removal.

no carbon dioxide. We can therefore exclude direct cyclic termination on two counts. There is no acetyl peroxide produced during termination (less than 6% of termination), and there is carbon dioxide produced.[24,25] Demonstration that this carbon dioxide is related to termination is the subject of the following paper in this issue.

Previous studies of gas-phase, photoinitiated acetaldehyde autoxidation using ^{18}O-labeling studies seemed to indicate one oxygen evolved per termination step, consistent with reaction 22. However, under the conditions of this study by McDowell and Sifniades, the chain length was between 1 and 2. At these chain lengths, the only reaction occurring was probably methyl and formyl radical oxidation (eq 25 and 26). Interaction of methylperoxy radicals pro-

$$CH_3CHO \xrightarrow{h\nu} CH_3\cdot + \cdot CHO \tag{25}$$

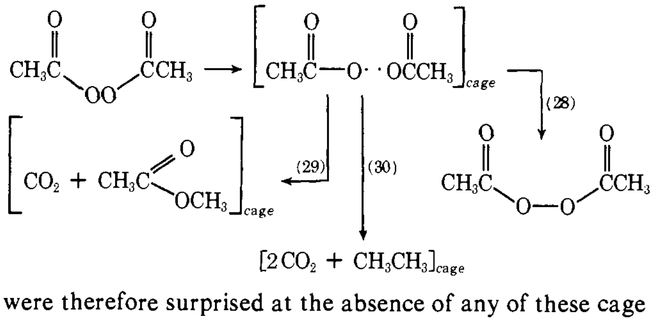
$$2\,CH_3\cdot + {}^{18}O{}^{18}O + {}^{16}O{}^{16}O \longrightarrow CH_3{}^{18}O{}^{18}O\cdot + CH_3{}^{16}O{}^{16}O\cdot \tag{26}$$

duces one oxygen per interaction (eq 27).[6b] Thus the results

$$CH_3{}^{18}O{}^{18}O\cdot + CH_3{}^{16}O{}^{16}O\cdot \longrightarrow {}^{16}O{}^{18}O + CH_3OH + CH_2O \tag{27}$$

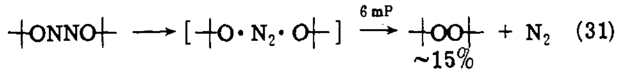
of McDowell and Sifniades[17] can be explained without a cyclic process.

The Absence of Cage Termination. As we shall show in following papers in this issue, oxygen is evolved along with CO_2 evolution. This result demands a head-to-head interaction of acetylperoxy radicals according to reaction 12 and those which follow. We expected some acetyl peroxide and methyl acetate from reactions 13 and 16 by analogy with the reactions of acetyl peroxide itself (eq 28-30).[20-22] We



were therefore surprised at the absence of any of these cage products.

We are consequently faced with two problems. First, why does acetyl tetroxide not give any of these cage products? We know from previous work that an intervening O_2 or N_2 molecule lowers the cage reactions by only about 30% (eq 31 and 32).[26] Yet the introduction of an extra two atoms



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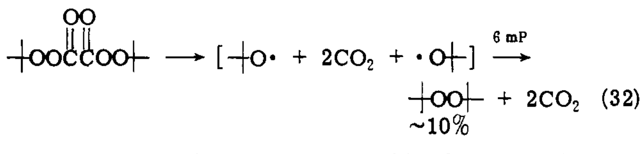
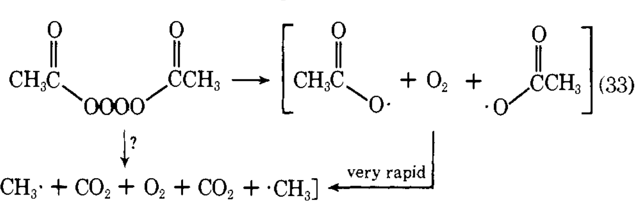


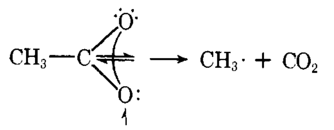
(32)

into acetyl peroxide to form a tetroxide *eliminates* the cage products. Note that, although we set 7% as an upper limit of methyl acetate production, we know that, in acetyl peroxide decomposition, there is about twice as much methyl acetate cage product as ethane cage product.[20] Therefore acetyl peroxide is probably less than 3% of termination.

Since we hesitate to resort to probability effects to explain the absence of cage products, we are left with the energetics of the decomposition. The very exothermic decomposition of acetyl tetroxide could result in a nearly concerted cleavage of all bonds (eq 33). Although no cage reactions



having three intervening molecules have been studied, we would expect a small amount of ethane from the cage in reaction 33. It seems necessary to postulate some excess translational energy in the methyl radicals and to postulate other unusual cage species such as the σ-acetoxy radicals which would decompose more rapidly than do π radicals.



(34)

The second question is the nature of the termination itself. If termination doesn't occur as part of the acetylperoxy radical interaction, it must occur afterward. We therefore conclude that termination takes a course similar to that in cumene autoxidation in which methylperoxy radicals are in-

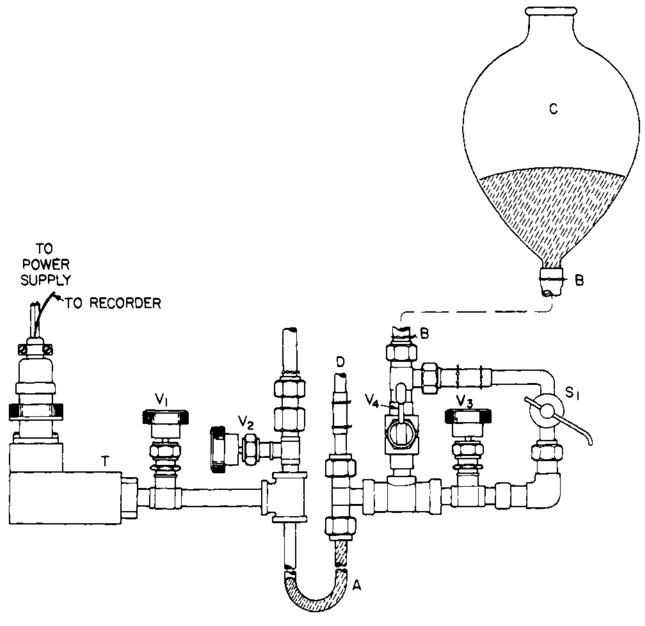
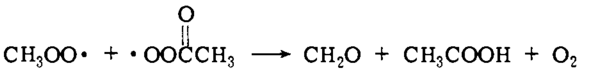


Figure 5. Apparatus for recording gas evolution or absorption using feedback control. See text for description.

volved.[6] Thus, in analogy to reaction 11 for cumene, we could write two terminating processes (eq 20 and 21). The

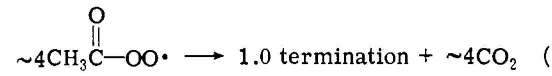
$$CH_3OO\cdot + \cdot OOCH_3 \longrightarrow CH_2O + CH_3OH + O_2 \quad (21)$$



$$CH_3OO\cdot + \cdot OO\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_2O + CH_3COOH + O_2 \quad (20)$$

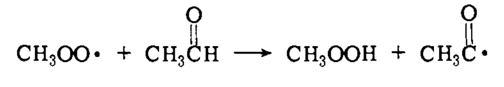
finding of 28% methanol in the product suggests that termination occurs 28% of the time by reaction 21 and the rest by reaction 20. Acetic acid, which should appear from reaction 20, is also a product of the peracid oxidation of acetaldehyde (eq 23) and cannot be used to probe for reaction 20.

We had previously demonstrated for cumene autoxidation that not all peroxy radicals lead to termination.[6] We now find a rather similar situation in which more than the required two molecules of carbon dioxide are evolved for each termination (eq 35). In the case of cumene autoxida-



$$\sim 4CH_3\overset{O}{\overset{\|}{C}}—OO\cdot \longrightarrow 1.0 \text{ termination} + \sim 4CO_2 \quad (35)$$

tion, both cumyloxy radical and methylperoxy radicals could continue the chain by abstraction.[27] In the present situation, the chain could easily be carried by methylperoxy radical, because abstraction from acetaldehyde is faster than that from cumene.[2] The product data reported here strongly support chain termination of acetaldehyde by the methylperoxy radical interactions 20 and 21 accompanied by some chain continuation by reaction 36.



$$CH_3OO\cdot + CH_3\overset{O}{\overset{\|}{C}}H \longrightarrow CH_3OOH + CH_3\overset{O}{\overset{\|}{C}}\cdot \quad (36)$$

The quantitative studies of carbon dioxide evolution in the following paper in this issue further define and document these processes.

Experimental Section

Materials. All aldehydes except pivaldehyde (Baker) were purchased from Aldrich, stored at −20° under argon, and all purified immediately before use by distillation under argon at atmospheric pressure.

Benzene (Mallinckrodt, thiophene-free) was purified by stirring with concentrated sulfuric acid, washing, drying, distilling, and pouring through an activity 1 neutral Woelm alumina. It was redistilled before use.

Table IV. GLC Columns

Column	Length, ft × diameter, in.	Packing
1	10 × $^1/_8$	Porapak QS (50–80 mesh)
2	20 × $^1/_8$	20% Carbowax 20M on Chromosorb P
3	6 × $^1/_4$[a]	10% diisodecyl phthalate on fluoropak 80 (40–60 mesh)
4	6 × $^1/_4$[a]	Porapak QS (50–80 mesh)
5	40 × $^1/_8$	20% XF-1150 on Chromosorb P
6	10 × $^1/_8$	Porapak Q (120–150 mesh)

[a] All-glass column.

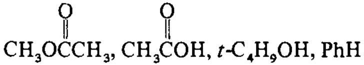
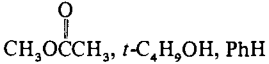
Di-*tert*-butyl peroxyoxalate (DBPO) was prepared as previously described.[14,19] *Note its treacherous explosive nature!*

Dimethyl peroxide (DMP), prepared by the method of Magelli and Sheppard[28] and distilled as prepared through a calcium chloride drying tube into a cold trap, was contaminated with up to 70% dimethyl ether. Both were identified by tandem gas-liquid chromatography–mass spectroscopy. DMP had the following relative peak heights: *m/e* (peak height) 14 (2.9), 15 (20), 17 (2.1); 18 (9.2), 28 (23), 29 (89), 30 (36), 31 (100), 32 (31), 61 (5.2), 62 (53) (parent).

Acetyl peroxide was a commercial (K & K Chemical Co.), 25% solution in dibutyl phthalate. Other chemicals were standard reagent grade materials.

Apparatus. Gas-liquid phase chromatographic analyses (GLC) were performed on a Hewlett Packard F & M Model 7000 chromatograph, using thermal conductivity except for ethane analysis in which flame ionization detection was used. An LKB Model 9000 gas chromatograph–mass spectrometer was used to perform GLC–MS measurements. Oxygen evolution at constant pressure or constant volume was measured using the apparatus shown in Figure 5 which is a revised version of that previously described.[14b] Instead of the solenoid valve used previously to allow mercury to flow into the gas buret (attached at D), we now employ a Teflon stopcock (S_1) which is turned by a 12-in. arm attached through a pivot to the penholder on a Heathkit recorder. In a separate sensing arm attached to the reactor, the contact I in Figure 4 of ref 14b is replaced by a penlight-photocell apparatus in which the mercury meniscus passes between the light and the photocell to decrease or increase the output voltage (~200 mV) of the photocell. Because this output voltage drives the pen on the Heathkit recorder, any decrease in pressure in the reactor proportionally opens the stopcock S_1 allowing mercury to flow into the gas buret, restoring the gas pressure in the reactor to its original value. Thus, the Heathkit recorder serves as a feedback proportional-type pressure controller. The amount of gas is, as before, recorded on a separate strip chart recorder which records the output of the pressure transducer T. Other than these changes, the operation is as previously described. If the stopcock S_1 is kept closed and D attached to the reactor, then the transducer T records reactor pressure changes directly, and rates of gas absorption at constant volume can be calculated from the pressure change. We have used this device in both ways. In the constant-volume mode, the recorded transducer output is separately calibrated with the reactor in moles of gas/division by injecting known volumes of gases into the reactor and observing the chart output. Oxidations are carried out at 25° as previously described. The volume of the liquid phase in these reactions was usually 19.78 ml and that in the gas phase 69.71 ml. Conditions shown in Table I were maintained by temporarily adjusting the pressure to 1 atm every 1000 sec, injecting 0.2150 ml of aldehyde and following the pressure change again. In this way, the use of metal needles could be avoided and plastic needles inserted through a 1-mm bore stopcock. In order to inject small quantities of liquid without gas loss, polyethylene needles were designed so that the shoulder of the needle could be pressed against the end of the glass tube attached to the stopcock through which the injection is made, thus making a gas-tight seal. The pressure in the reactor was first carefully adjusted to 1 atm by manually moving an attached mercury column, then the stopcock opened, and the needle quickly inserted. After injection, the pressure was again adjusted to 1 atm, the needle quickly removed, and the stopcock closed.

Table V. Instrumental Conditions for Various GLC[a] and GLC–MS Analyses[b]

Analysis	Column[d]	Column temp., °C		
		At start	After (min)	
GLC[c]	1	−10	Same	$N_2(O_2)$, CH_4, CO_2
GLC[c]	6	25	Same	$N_2(O_2)$, CH_4, CO, CO_2, C_2H_6
GLC[d]	5	150	Same	 $CH_3O\overset{\overset{O}{\parallel}}{C}CH_3$
GLC[c]	3	75	Same	CH_3OCH_3, $CH_3OOCH_3(CH_3CHO)$
GLC–MS[d]	4	110	150 (12)	CH_3OH, CH_3OCH_3, CH_3OOCH_3,  $CH_3O\overset{\overset{O}{\parallel}}{C}CH_3$, $CH_3\overset{\overset{O}{\parallel}}{C}OH$, t-C_4H_9OH, PhH
GLC–MS[d]	4	100	150 (18)	CH_3CHO, C_2H_5CHO, C_2H_5OH,  $CH_3O\overset{\overset{O}{\parallel}}{C}CH_3$, t-C_4H_9OH, PhH
GLC–MS[d]	4	85	120 (20)	Acetone (2-propanol), i-C_3H_7 CHO (t-C_4H_9OH)
GLC[d]	1	120	Same	Acetone, 2-propanol, pentane, i-C_3H_7CHO (t-C_4H_9OH)

[a] GLC detector temperature = 190°, injector temperature = variable, flow = ~25 cm^3/min at 40 psi He. [b] Flow 25–30 cm^3/min at 40 psi He. [c] Gas phase analyzed. [d] Solution analyzed.

In addition, rates were measured near 1 atm pressure to avoid a changeover to R· + ROO· termination which occurs in aldehyde oxidations at lower pressures of oxygen.[2,3]

In those cases where total peroxide concentration was desired, a small aliquot of solution was withdrawn using a polyethylene needle as described above, prior to addition of the aliquot of aldehyde, and titrated with iodide by standard methods. Results of combined oxygen uptake-peroxide titration experiments thus obtained are shown in Figures 2, 3, and 4. Carbon dioxide yields were obtained as described in detail in the following paper in this issue.

GLC and GLC-MS Conditions. The columns used for product analyses are listed in Table IV, and the operating conditions and substances analyzed are shown in Table V. Because one *t*-BuOH is produced for each 0.87 radical initiated from DBPO and is not consumed during autoxidation, it could be used as a standard for comparison in all solution-phase analyses. We have used a direct comparison of *tert*-butyl alcohol peak heights with those of methanol, methyl acetate, acetone, and isopropyl alcohol in the liquid-phase analyses. In some cases, pentane was added as an additional standard. As a standard for gas-phase analyses, aliquots of methane were injected into the reactor as described above. A comparison of the carbon dioxide, ethane, methyl peroxide, etc. peak areas with that of methane allows the yield of these gases to be calculated. To further document this method in, e.g., the case of ethane, known amounts of ethane were injected into the reactor after the "product ethane" had been searched, and a comparison of the ethane to the standard methane peak areas was made.

Products such as methanol, methyl peroxide, etc., which are listed in Table V as analyzed by GLC-MS, were easily identified by their mass spectral patterns.

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