Aldehyde Autoxidation. II.[1] Carbon Dioxide Evolution[2]

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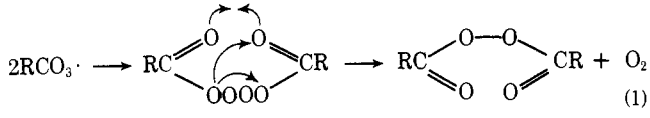
Abstract: Carbon dioxide is evolved during radical catalyzed autoxidation of aliphatic aldehydes. The amount of carbon dioxide is independent of kinetic chain length but varies greatly with the structure of the aldehyde. There are from two to ten carbon dioxides evolved per terminating radical. This is interpreted as evidence for the reaction of acetylperoxy radicals to produce, through a tetroxide, methyl radicals which can either terminate or propagate chains.

Because we found in the previous paper insufficient acetyl peroxide, dimethyl peroxide, methyl acetate, and ethane to account for termination, we concluded that aldehyde termination occurred in neither cyclic processes[3] (eq 1) nor as



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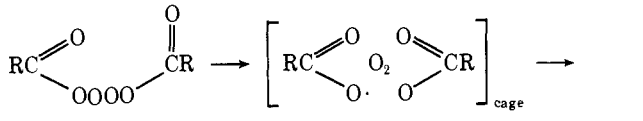
a result of cage collapse (eq 2). The evolution of carbon



$$[\text{products}]_{\text{cage}} \quad (2)$$

dioxide and methanol suggested the possibility of a direct formation of noncage radicals from the tetroxide (eq 3),

(3)

with subsequent termination by methylperoxy radicals[4,5] (or ROO· in the general case) (eq 4). But the methylperoxy

$$2CH_3OO\cdot \longrightarrow CH_2O + CH_3OH + O_2 \quad (4)$$

radical could also reenter the chain[6] (eq 5) and, as a result,

$$CH_3OO\cdot + CH_3CHO \longrightarrow CH_3OOH + CH_3\dot{C}O \quad (5)$$

not all carbon dioxide evolving interactions (3) would lead to termination. In fact, if this termination behaves like that of cumene,[4] there would be more carbon dioxide evolved per termination as the acetaldehyde concentration increases because methylperoxy radical would be caused to propagate rather than terminate.

We therefore studied the rate of carbon dioxide evolution during aldehyde autoxidation under various conditions.

Experimental Section

Materials used are described in the previous paper.[1]

Apparatus for Simultaneous Measurement of Oxygen Uptake and Carbon Dioxide Evolution Rates. Because chain lengths were usually long,[7] the oxygen uptake was measured by pressure change using the pressure transducer previously described.[1,5] The relatively small amount of carbon dioxide evolved was determined by gas–liquid chromatography using methane as an internal standard.

The apparatus is shown in Figures 1, 2, and 3. The reaction flask shown in Figure 1 is connected to the glass valving system (Figure 2) via an 18–9 ball joint labeled J_1 and J_2. This assembly is connected into a modified F & M Model GV-11 gas sampling valve through stainless steel tubing as indicated by "Sample In" connector H_2 and "Sample Out" connector H_1. The sampling valve is attached to the gas chromatograph[2] equipped with column 1 of Table IV in the previous paper in this issue. A mercury column is connected to the bulb in Figure 2 below E. This mercury column is maintained at E during oxygen uptake and, because the mercury column is connected to the pressure transducer (range 1 atm), the pressure in the reactor can be monitored continuously. The total volume of the reactor plus glass valving assembly plus the gas sampling valve was determined to be 89.53 ml when the mercury column was at E and V_{in}, V_{out} and S_3 open, S_4 open to J_3, S_2 closed, and J_3 capped with a syringe cap. Therefore the pressure in the gas (89.53 ml − V_{liquid}) phase can be used to calculate the amount of oxygen present, after a small correction is made for the solubility of oxygen in the liquid. No correction is made for solvent vapor pressure, because we need only monitor the pressure change. Pressures recorded as transducer output on a mV recorder were calibrated in Torr before each run as previously described.

Oxygen Uptake. Both gas and liquid samples were introduced using accurately calibrated syringes with spacers[8] and, for liquids, only plastic needles. In a typical experiment, the flask in Figure 1 is maintained at 25°. With V_{in}, V_{out}, S_2, S_3, and S_4 open oxygen can be passed in at F and out at S_4 filling the entire apparatus. About 40 mg of di-*tert*-butyl peroxyoxalate is dissolved in 25.00 ml of benzene and 19.78 ml of this injected into the reactor. After flushing with oxygen for 5 min, S_2 is closed and a serum cap placed over J_3 to close the system. An accurately measured amount of methane gas is then injected through J_3 at 25° as a GLC standard. The methane is mixed with the rest of the gas by the pumping procedure described below.

At this point, the CO_2 evolution from initiator alone can be measured by using the mercury column at E to pump gases from the reactor through the tube G through the GLC loop 1 and into the bulb below E. This is done by closing valve S_3, having the line going from H_2 to H_1 connected to the loop 1 by opening V_{in} and V_{out}, having the plunger P_1 properly positioned, and quickly raising and lowering the mercury level in the bulb ten times so as to assure that a representative gas sample in the reactor finds itself in 1. Then V_{in} and V_{out} are closed, the time recorded on the recorder and the plunger P_1 then pulled to inject this sample into the GLC in the usual way. A comparison of the CO_2 and methane peak areas reveals the ratio of these gases in the sample.

To avoid introduction of high-pressure helium into the reactor from 1, the V_{in} and V_{out} valves are left closed after the injection, P_1 is returned to its original position, and the sample loop is vented through "Vent" to 1 atm. In this way, the sample removed from the reactor (2 ml of gas) gets replaced with an equal volume of helium. This limits us to about 15 meaningful samples of CO_2 because, after 15 samples, helium pressure in the reactor is such that the oxygen pressure is less than $\frac{2}{3}$ atm.

After initiator evolution of CO_2 has been followed as long as desired, the autoxidation is started by injecting 0.3857 ml of aldehyde by methods previously described. During this and subsequent injections of 0.213 ml of aldehyde each 10^3 sec, care is taken to prevent losses of any gas over the solution. The mercury level is returned to E and the pressure in the reactor brought to 1 atm by quickly admitting oxygen through S_2 and S_3 every time the total

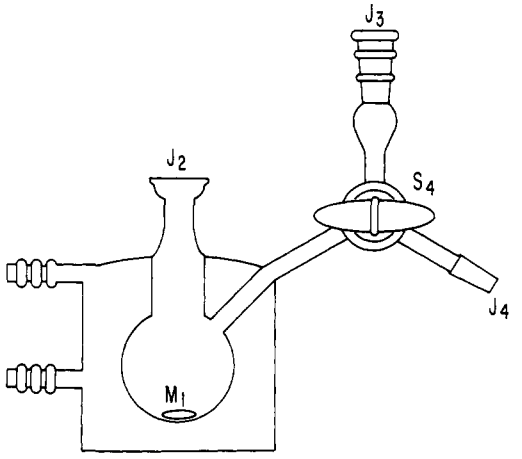


Figure 1. Reaction flask used in determining pressure changes and carbon dioxide evolution for aldehyde autoxidations.

pressure gets below about 600 Torr. Between interruptions due to CO_2 sampling and aldehyde injections, the pressure change is continuously recorded with the pressure transducer activated by the mercury column at E. For this purpose, S_3 is open at all times except during CO_2 sampling.

Treatment of Data

Oxygen Uptake. Because there were interruptions, the pressure change recordings were a series of short plots. Because the recorder runs continuously, it is quite easy to extrapolate these segments together into a single accurate dP/dt plot. The pressure change is principally due to oxygen disappearance at long chain length, and thus we set $(dP/dt)V/RT$ = moles of oxygen/sec and express this as M/l. solution per sec by dividing by 0.01938 l. of solution.

Carbon Dioxide Evolution. Because of some difficulties involved in transferring methane for purposes of standardization, we used the known rate of CO_2 evolution from DBPO to afford an internal CO_2 standard. Because the rate of CO_2 evolution from DBPO has been measured several times by mass spectra and GLC and shown to correlate with rates measured by other methods,[9] we took as the rate of CO_2 evolution from initiator the k_{decomp} × concentration of DBPO. Thus using the amount of methane injected as an uncorrected standard, we can determine from GLC peak height ratios H_{CO_2}/H_{CH_4} the $d[CO_2]/dt$ before and after the first aldehyde additions. Then, setting the slope before aldehyde addition equal to k_{decomp} × concentration of DBPO, we get the rate of CO_2 from termination as well.

Because 2 ml of each gas i are removed from V_i' ml [89.53 ml plus the effective gas volume in the liquid, 20 ml benzene, or $V_i' = V_{gas} + V_{liq} \times$ solubility of gas i (ml/ml liquid)], the fraction of methane remaining would be

$$\frac{V_{CH_4}' - 2}{V_{CH_4}'}$$

Therefore the amount of methane remaining before point n, $[CH_4]_n$, is given by eq 6. The amount of CO_2 determined at

$$[CH_4]_n = \left(\frac{V_{CH_4}' - 2}{V_{CH_4}'}\right)^{n-1} [CH_4]_0 \qquad (6)$$

point n in $[CO_2]'_n$ is given by the ratio of peak heights times the molar sensitivity ratio, sens, times eq 6 (see eq 7)

$$[CO_2]_n' = [CH_4]_n \left(\frac{H_{CO_2}}{H_{CH_4}}\right)_n \text{sens} \qquad (7)$$

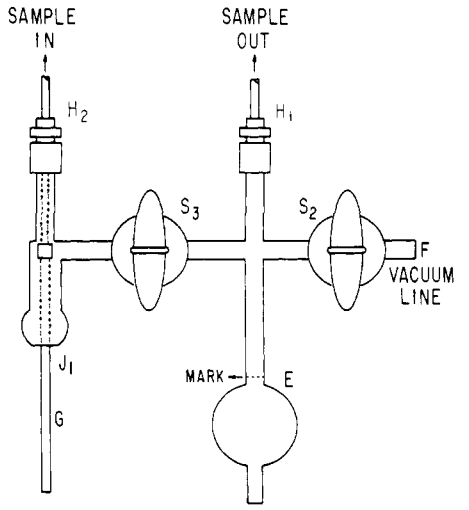


Figure 2. Glass valving system. The inner tube G is glass, but the outer connectors H_1 and H_2 are swagelock to stainless steel tubing. See text.

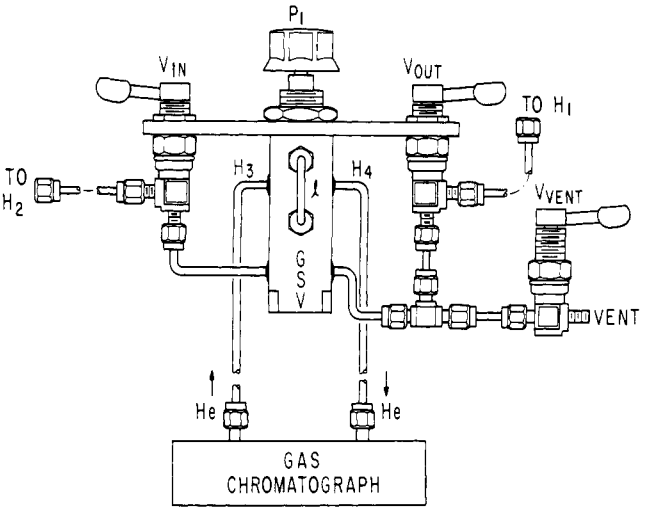


Figure 3. Modified gas sampling valve for gas–liquid chromatography used in determining carbon dioxide evolution for aldehyde autoxidations.

which must be corrected by adding the cumulative amount of CO_2 removed. The total CO_2 evolved then becomes:

$$[CO_2]_n = [CO_2]'_n + \left(\frac{2}{V_{CO_2}'}\right) \sum_{n=1}^{n} [CO_2]'_{n-1} \qquad (8)$$

where $[CO_2]'_n$ and $[CO_2]'_{n-1}$ are obtained from eq 7. This determination is not particularly changed if both V_{CO_2}' and V_{CH_4}' are set equal to V_{gas} = 69.1 ml, because errors introduced by this assumption tend to cancel out. The corrections for removal are about 20% for methane and 10% for CO_2 after ten samples have been taken. Therefore the accuracy of CO_2 determination is not very sensitive to inaccuracies in these corrections. All gas quantities in total moles contained are divided by the volume of liquid and all concentrations thus expressed as total mol/l. of solution. The concentrations of carbon dioxide thus determined (without sensitivity correction) are plotted vs. time in the indicated figures.

In those cases where initiator CO_2 evolution is not measured, the slopes are taken as total CO_2 evolution from which calculated $(d[CO_2]/dt)_{init}$ are subtracted to give that arising from autoxidation. Otherwise, the slopes before (Slope I) and after aldehyde addition (Slope II) can be

Table I. Aldehyde Autoxidation Rates and Carbon Dioxide Evolution Rates

Aldehyde	R_i,[a] M sec^{-1} × 10^7	d[O_2]/dt, M sec^{-1} × 10^5	Chain length[b]	CO_2 evolution[c] Slope I, M × 10^7	CO_2 evolution[c] Slope II, M × 10^7	CO_2 per termination step[d,e]
CH_3CHO	1.74	7.5	430	1.8	5.69	5.0
CH_3CHO[f]	1.77	~5	~300	1.86	5.90	5.0
C_2H_5CHO	1.69	6.29	370	1.22	6.93	10.7
i-C_3H_7CHO	1.57	5.66	360	1.89	20.1	22
$C_6H_{11}CHO$	1.68	4.80	285	0.80	9.4	24

[a] R_i ≡ concentration of DBPO × 1.41 × 10^{-5} sec^{-1} × 0.87 × 2. [b] Chain length = d[O_2]/dt/R_i. [c] See Figures 1–3 for difinitions of these slopes. These experiments were carried out several times with similar results. Representative data are shown here. [d] CO_2 per termination = 2(Slope II − Slope I)/0.87 Slope I. See text. [e] The reproducibility of these values is actually only ±10% over several runs. [f] This experiment was done with syringe sampling of gases for GLC.

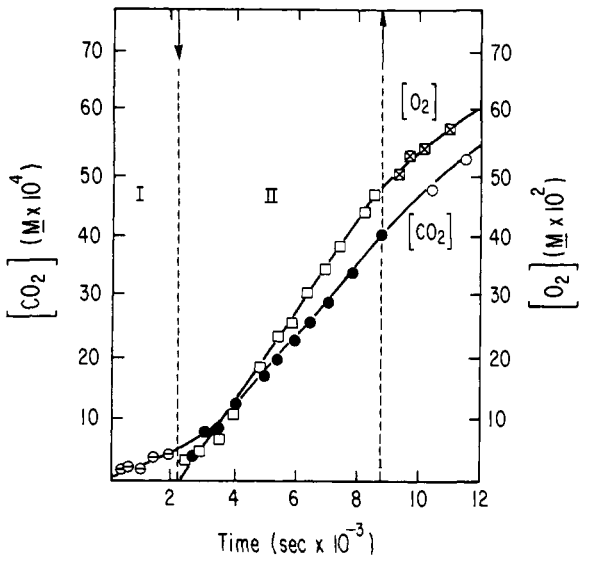


Figure 4. Plots of oxygen absorbed and carbon dioxide evolved during and before the autoxidation of acetaldehyde in benzene at 25°, concentration of DBPO = 7.09 × 10^{-3} M. The first addition of aldehyde, 0.386 ml at 2250 sec ↓, was followed by addition of 0.2130 ml every 1000 sec until 8600 sec ↑. ○, CO_2 evolved. Slope I, 1.87 × 10^{-7} M sec^{-1}. Slope II, 5.69 × 10^{-7} M sec^{-1}. □, oxygen uptake. Rate during 2–8 × 10^3 sec (period II), 7.46 × 10^{-5} M sec^{-1}.

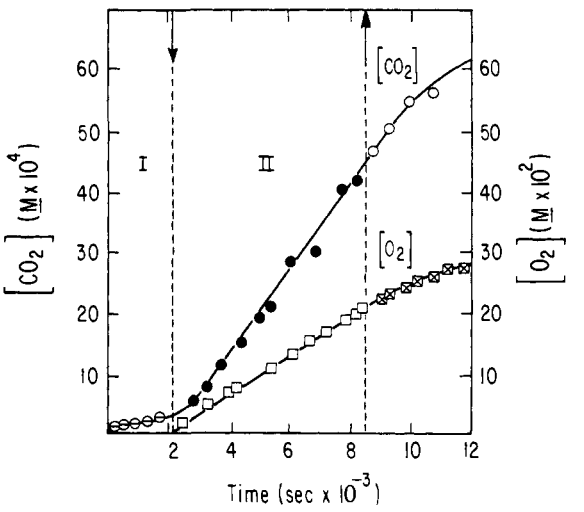


Figure 5. Plots of oxygen absorbed and carbon dioxide evolved during and before the autoxidation of propionaldehyde in benzene at 25°. Concentration of DBPO = 6.91 × 10^{-3} M. The first addition of aldehyde, 0.386 ml at 2200 sec ↓, was followed by additions of 0.2130 ml every 1000 sec until 8500 sec ↑. ○, CO_2 evolved. Slope I, 1.22 × 10^{-7} M sec^{-1}. Slope II, 6.93 × 10^{-7} M. □, oxygen uptake. Rate during period II, 6.29 × 10^{-5} M sec^{-1}.

combined with the calculated rate of initiator CO_2 evolution $(d[CO_2]/dt)_{init}$ to determine rate of CO_2 evolution from autoxidation $(d[CO_2]/dt)_{aut}$ (see eq 9). The number

$$\left(\frac{d[CO_2]}{dt}\right)_{aut} = (\text{Slope II} - \text{Slope I})\frac{(d[CO_2]/dt)_{in}}{\text{Slope I}}$$

$$= (\text{Slope II} - \text{Slope I})\frac{2[\text{DBPO}]k_{in}}{\text{Slope I}} \quad (9)$$

of carbon dioxide molecules per terminating pair is then given by this rate divided by the initiation rate

$$CO_2 \text{ evolved per initiating pair} = 2(d[CO_2]/dt)_{aut}/R_i \quad (10)$$

where R_i, the rate of production of radical chains, is

$$R_i = 2k_{in} \times \text{Eff} \times [\text{DBPO}] \quad (11)$$

At 25° in benzene, k_{in} for DBPO is 1.41 × 10^{-5} sec^{-1},[9] and the efficiency is 0.87.[10] Concentrations of DBPO were usually around 7 × 10^{-3} M. For simplicity, if we set Slope I ≡ k_{in} × [DBPO], then the number of CO_2 molecules per termination is

$$CO_2/\text{terminating pair} = 2(\text{Slope II} - \text{Slope I})/(\text{Slope I} \times \text{Efficiency}) \quad (12)$$

Results

Effect of Aldehyde Structure on CO_2 Evolution. Typical plots of concentrations of oxygen and carbon dioxide vs. time, determined as above, are shown in Figures 4–6 for the autoxidation of three aldehydes. The data for these aldehydes are tabulated in Table I.

Effect of Aldehyde Concentration. To determine whether aldehyde concentration affects carbon dioxide yields by contributing to the competition of reactions 4 and 5, the acetaldehyde autoxidation of Figure 4 was repeated with two variations. The 0.387 ml of aldehyde was added along with DBPO, and no further aldehyde was added. As the aldehyde was consumed, the reaction slowed down. Therefore, tangents to the d[O_2]/dt plot were taken at intervals and these tangents plotted vs. time in Figure 7. The same plot shows total carbon dioxide evolution and the calculated evolution from initiator only. It is clear from this plot that decreasing aldehyde concentration does not decrease carbon dioxide evolution.

Effect of Cooxidants upon CO_2 Evolution. The termination of tetralylperoxy radicals is about as fast as that of acetylperoxy radicals,[11] and thus cooxidation with tetralin should lead to a change in termination mechanism with consequent decrease in CO_2 evolution. On the other hand, termination by *tert*-butylperoxy radicals is very slow (~3 × 10^{-2} M^{-1} sec^{-1}).[11] Therefore, even in the presence of *tert*-butyl hydroperoxide, the termination of acetaldehyde aut-

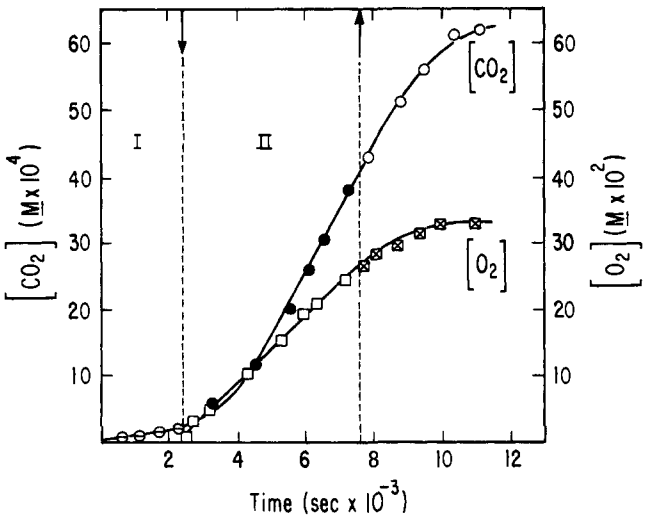


Figure 6. Plots of oxygen absorbed and carbon dioxide evolved during and before the autoxidation of cyclohexane carboxaldehyde in benzene at 25°. Concentration of DBPO = 6.84×10^{-3} *M*. The first addition of aldehyde, 0.386 ml ↓, was followed by additions of 0.2130 ml at 1000 sec intervals until 7750 sec ↑. ○, CO_2 evolution. Slope I, 0.80×10^{-7} *M* sec^{-1}. Slope II, 9.4×10^{-7} *M* sec^{-1}. □, oxygen uptake. Rate during period II, 4.80×10^{-5} *M* sec^{-1}.

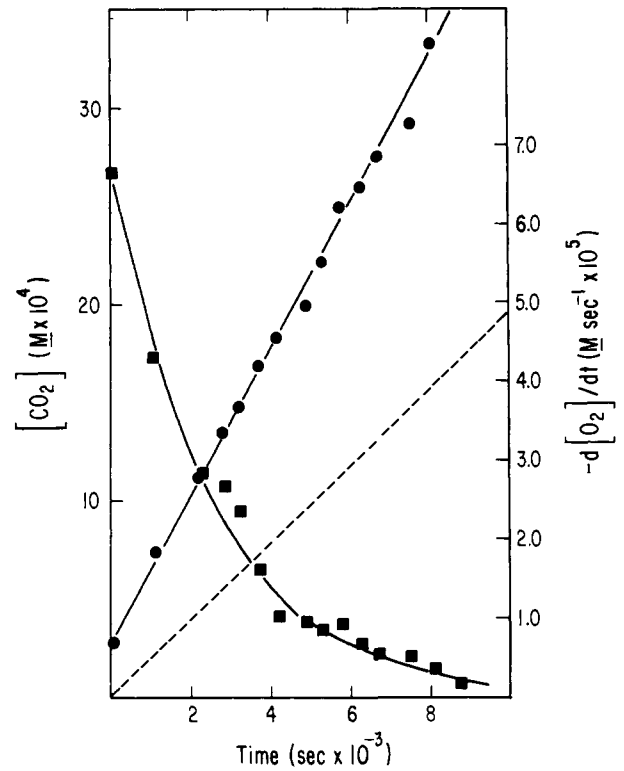


Figure 7. Carbon dioxide evolution and rates of oxygen absorption vs. time during acetaldehyde autoxidation in benzene at 25°. One addition only of 0.36 ml of aldehyde was made at zero time (~0.3 *M*). ■, $(d[O_2]/dt)$ vs. time. ●, CO_2 concentration (total mol/l. of solution) vs. time. - - -, calculated concentration of CO_2 vs. time from initiator decomposition.

oxidation should still proceed by the rapid ($\sim 10^8$) acetylperoxy radical interaction. These possibilities were tested by carrying out acetaldehyde autoxidation as described in Figure 4 except that, after a certain period, either tetralin or *tert*-butyl hydroperoxide was added. In both cases, the rate of oxidation decreased. The plots of carbon dioxide concentration vs. time for these experiments are shown in Figure 8. It is clear that both tetralin at low concentration and *n*-hexane as solvent decreased the CO_2 evolution rates. However, the addition of 0.3 *M* *tert*-butyl hydroperoxide, which decreased the chain length by a factor of 10, did not affect CO_2 evolution. In fact, 0.82 *M* *tert*-butyl hydroperoxide does not change the rate of CO_2 evolution.

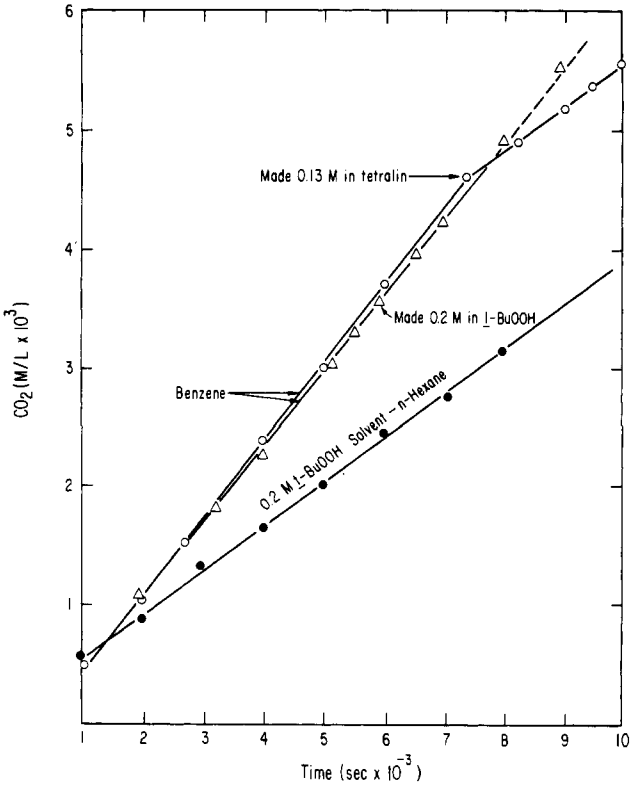


Figure 8. Carbon dioxide evolution during acetaldehyde autoxidation in benzene or *n*-hexane at 25° with 7.0×10^{-3} *M* DBPO initiator. After 0.36 ml of acetaldehyde was added at zero time, 0.21 ml was added each 1000 sec to keep the aldehyde concentration at 0.3 *M*. ○, solvent benzene, tetralin to make the solution 0.13 *M* was added at 7400 sec. △, solvent benzene, 25°. Sufficient *tert*-butyl hydroperoxide to make the solution 0.2 *M* was added at 5700 sec. ●, solvent, *n*-hexane, 0.2 *M* *tert*-butyl hydroperoxide. The 0.21 ml aliquots of aldehyde were omitted. Similar effects were observed when tetralin or *tert*-butyl hydroperoxide was included in the solvent at zero time.

Discussion

The first thing we learn from these studies (Table I) is that five CO_2 molecules are evolved for every terminating pair in acetaldehyde autoxidation. This is three more than required if all methyl radicals terminated (eq 13) or five

$$CH_3OO\cdot + \cdot OOR \longrightarrow CH_2O + ROH + O_2 \quad (13)$$

more than required if the acetylperoxy radicals gave acetyl peroxide directly. Therefore some chain propagation after CO_2 evolution must be occurring (reaction 5). That the number of carbon dioxide molecules per termination increases with branching in the aldehyde is also consistent with this notion, because termination rates of primary alkylperoxy radicals (eq 14) are faster ($\sim 10^8$ M^{-1} sec^{-1}) than

$$2RCH_2OO\cdot \longrightarrow RCHO + RCH_2OH + O_2 \quad (14)$$

those of secondary peroxy radicals (e.g., cyclohexylperoxy radical 1.6×10^6 M^{-1} sec^{-1})[11] (see eq 15). This means that

$$2R_2CHOO\cdot \longrightarrow R_2CO + R_2CHOH + O_2 \quad (15)$$

the secondary peroxy radicals would be relatively more prone to carry out propagation (eq 16), because the propagation reaction is not very sensitive to alkyl structure.[7] It is not clear that the rate of tetroxide decomposition, even if it

Table II. Propagation and Termination Rate Constants for Selected Peroxy Radical Forming Substrates

	Substance			
	t-BuOOH	Cumene	Tetralin	Acetaldehyde
k_p, M^{-1} sec^{-1}:	12[a]	0.2[c]	4.6[b]	2700[c,d]
k_t, M^{-1} sec^{-1}:	3×10^2 [b]	1.9×10^4 [b]	4×10^6 [b]	5×10^7 [c,d]

[a] J. R. Thomas and C. A. Tolman, *J. Am. Chem. Soc.*, 84, 2079 (1962). [b] Reference 11. [c] J. A. Howard in "Advances in Free Radical Chemistry", Vol. IV, G. A. Williams, Ed., Academic Press, New York, N.Y., 1972, p 49. [d] Reference 12.

$$R_2CHOO\cdot + R_2\overset{H}{\overset{|}{C}}HCO \longrightarrow R_2CHOOH + R_2\dot{C}HCO \quad (16)$$

were sensitive to aldehyde structure, would affect the CO_2 evolution, because all acyloxy radicals decompose and escape the cage, even in the case of acetylperoxy radicals.

Effects of Cooxidants. Possible effects of additives upon acetaldehyde autoxidation rates and termination product yields are predictable from the rate constants in Table II. The addition of *t*-BuOOH to cumene autoxidation mixture would affect propagation only slightly, but *t*-BuO· rather than cumyloxy radicals would be produced by reaction 17.

$$2ROO\cdot \longrightarrow [2RO\cdot + O_2] \xrightarrow[10\%]{b} ROOR \quad (17)$$

(a: $\longrightarrow 2RO\cdot$)

Because *t*-BuO· does not fragment under these conditions, methylperoxy radicals cannot be produced, termination is retarded, and the rate should increase. This result has been reported.[5]

Addition of *t*-BuOOH to acetaldehyde autoxidation mixtures results in chain transfer as in the cumene case (eq 18). This leads to a propagation step (eq 19), which is much

$$t\text{-BuOOH} + CH_3\overset{O}{\overset{\|}{C}}\text{—}OO\cdot \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OOH + t\text{-BuOO}\cdot \quad (18)$$

$$t\text{-BuOO}\cdot + CH_3CHO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\cdot + t\text{-BuOOH} \quad (19)$$

slower than the normal propagation (eq 20). This slower

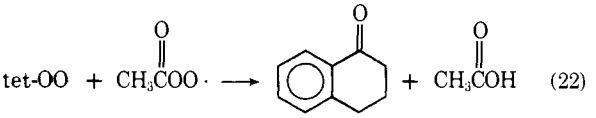
$$CH_3\overset{O}{\overset{\|}{C}}OO\cdot + CH_3CHO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OOH + CH_3\overset{O}{\overset{\|}{C}}\cdot \quad (20)$$

propagation should slow the rate. However, the rate of termination of *tert*-butylperoxy radicals is so slow that it is unlikely to be competitive with that of AcOO· at any reasonable concentration such as 0.3 *M* in both acetaldehyde and *tert*-butyl hydroperoxide. Furthermore, because neither the interaction of *t*-BuOO· with itself or with $CH_3OO\cdot$ produces carbon dioxide, and because the self-reactions of *t*-BuOO· lead to only 10% termination (eq 17, paths a and c), neither process will appreciably affect carbon dioxide yields. It is therefore not surprising that, in Figure 8, the addition of *t*-BuOOH slows the rate while having *no effect* upon carbon dioxide evolution. Apparently the cross termination (eq 21) is also less favorable than is acetylperoxy

$$t\text{-BuOO}\cdot + AcOO\cdot \longrightarrow [AcOOOO\text{-}t\text{-Bu}] \longrightarrow \text{term.} \quad (21)$$

self-reaction. This finding makes possible the ^{18}O-labeling experiment described in the next paper in this issue.

On the other hand, k_t for tetralin is rather comparable to and k_p is less than those of acetaldehyde. Thus both the rate and carbon dioxide evolution are decreased, the latter due to the termination reactions (eq 22 and 23) which produce



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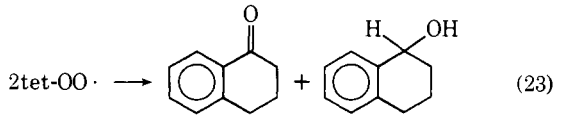

(23)

no carbon dioxide molecules. These results further support the suggestion that oxygen evolution is related to termination.

Relation of Carbon Dioxide Production to Termination Rates. The termination of cumene autoxidation was shown to involve more cumylperoxy radical interactions than terminations[4] [R = $PhC(CH_3)_2$] (eq 24). Because the cumyl-

$$R^{18}O^{18}O\cdot + ROO\cdot \longrightarrow R^{18}O^{18}OOOR \longrightarrow 2RO\cdot + {}^{18}O^{16}O \quad (24)$$

oxy radicals sometimes fragment into methyl radicals as mentioned above (eq 25), and these are very prone to termi-

$$\begin{matrix} CH_3 \\ | \\ PhCO\cdot \end{matrix} \longrightarrow CH_3\cdot + \begin{matrix} O \\ \| \\ PhCCH_3 \end{matrix} \xrightarrow{O_2} CH_3OO\cdot \quad (25)$$

nate, and because the cumyloxy (or methylperoxy)[6] radicals can also abstract hydrogen from cumene, the number of cumylperoxy radical interactions per termination is dependent upon cumene concentration. If cumene concentration is increased, more cumyloxy radicals abstract and thus propagate. This leads to more oxygen evolution (more ROO· interactions) per termination.[4]

However, Figure 6 clearly shows *no such dependence* for CO_2 evolution upon acetaldehyde concentration. The number of carbon dioxides evolving per unit time and thus per termination (constant initiation) is unaffected by a change from 300 to 30 in chain length. This corresponds to about a tenfold change in acetaldehyde concentrations. This is difficult to explain, because we have presented evidence that methylperoxy radicals both terminate and propagate in this system. This situation should be sensitive to aldehyde concentration, but it is not except at long reaction times where buildup of peracid, methyl hydroperoxide, and helium pressure along with sampling errors make our data less reliable. The rate of CO_2 evolution seems to be independent of aldehyde concentration under initial controlled conditions.

How then can abstraction from increased cumene by cumyloxy radical change the ratio of propagation to termination by this radical and yet the methylperoxy radical abstraction have no effect? The answer probably lies in the fact that reaction 26 is irreversible, and thus cumyloxy radi-

$$\begin{matrix} CH_3 \\ | \\ PhC\text{—}O\cdot \\ | \\ CH_3 \end{matrix} + \begin{matrix} CH_3 \\ | \\ PhC\text{—}H \\ | \\ CH_3 \end{matrix} \longrightarrow \begin{matrix} CH_3 \\ | \\ PhC\cdot \\ | \\ CH_3 \end{matrix} + \begin{matrix} CH_3 \\ | \\ PhCOH \\ | \\ CH_3 \end{matrix} \quad (26)$$

cal is removed from the system preventing MeOO· termination. However, the reaction 27 *is indirectly reversible.*

$$CH_3OO\cdot + CH_3CHO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\cdot + CH_3OOH \quad (27)$$

There is a virtual equilibrium between $CH_3OO\cdot$ and $AcOO\cdot$ through reaction 28. Therefore, even though acetaldehyde

$$CH_3C(=O)OO\cdot + CH_3OOH \longrightarrow CH_3OO\cdot + CH_3C(=O)OOH \quad (28)$$

concentration is increased, the concentration of $CH_3OO\cdot$ might not be appreciably changed.

If, on the other hand, the equilibrium reaction 28 dominates reaction 27 as it might when CH_3OOH builds up, then the CO_2 evolution would drop. This could occur at long reaction times.

In summary, the carbon dioxide evolution during aldehyde autoxidation responds to aldehyde structure and concentration and to added retarders in such a way as to document the proposed[1] aldehyde termination mechanism illustrated below for acetaldehyde.

$$2CH_3CO_3\cdot \longrightarrow$$

$$CH_3C(=O)OOOOC(=O)CH_3 \longrightarrow 2CH_3\cdot + 2CO_2 + O_2 \quad (29)[13]$$

$$CH_3\cdot + O_2 \longrightarrow CH_3OO\cdot \quad (30)$$

$$CH_3OO\cdot + AcH \longrightarrow Ac\cdot + CH_3OOH \quad (31)$$

$$CH_3OO\cdot + AcOO\cdot \longrightarrow CH_2O + O_2 + CH_3COOH \quad (32)$$

$$2CH_3OO\cdot \longrightarrow CH_2O + O_2 + CH_3OH \quad (33)$$

The relative importance of reactions 32 and 33 and further documentation of the proposed termination scheme are provided by the labeling experiments in the following paper in this issue.

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References and Notes

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Autoxidation of Acetaldehyde. III. Oxygen-Labeling Studies[1,2]

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Abstract: The autoxidation of acetaldehyde in solution at 25° was studied using a mixture of 95% $^{32}O_2$ and 5% $^{36}O_2$. From a comparison of the rates of $^{34}O_2$, $^{32}O_2$, $^{44}CO_2$, and $^{46}CO_2$ evolution, the numbers of oxygen and carbon dioxide molecules evolved for each termination step could be calculated. The results agree with the previous conclusion that the termination process is preceded by the formation of acetyl tetroxide which decomposes completely to methyl radicals, CO_2, and oxygen without appreciable cage collapse.

The interaction of acetylperoxy radicals and the consequent interaction of the derived methylperoxy radicals proposed in the two previous papers in this issue[2,3] demands the evolution of carbon dioxide and oxygen (eq 1 and 2). Furthermore, it is implied that the number of oxygens evolved be equal to one per termination process (pair) plus one for each two carbon dioxides evolved from reaction 1. Because di-*tert*-butyl peroxyoxalate is used as initiator, this means approximately one oxygen evolved per two total carbon dioxides evolved (eq 3). We have therefore employed the method of Bartlett and Traylor[4,5] using a mixture of $^{36}O_2$ and $^{32}O_2$ to determine these relationships (eq 4-10). From these reactions, we can determine not only evolved oxygen

$$CH_3C(=O)OOOOC(=O)CH_3 \longrightarrow 2CH_3\cdot + 2CO_2 + O_2 \quad (1)$$

$$2CH_3\cdot \longrightarrow 2CH_3OO\cdot \longrightarrow CH_2O + CH_3OH + O_2 \quad (2)$$

$$+OOCCOO+ \xrightarrow{Eff = 0.87} 2CO_2 + 2\,+O\cdot \quad (3)$$

initiation ← 87% | 13% → +OO+

$$DBPO \xrightarrow{0.87k_1} 2\,+O\cdot \longrightarrow CH_3C(=O)\cdot \quad (4)$$

$$CH_3C(=O)\cdot + {}^{36}O_2\ (5\%) \longrightarrow CH_3C(=O)-{}^{18}O{}^{18}O\cdot \quad (5)$$

$$CH_3C(=O)\cdot + {}^{32}O_2\ (95\%) \longrightarrow CH_3C(=O)-{}^{16}O{}^{16}O\cdot \quad (6)$$

$$CH_3C(=O)-{}^{16}O{}^{16}O\cdot + CH_3C(=O)-{}^{18}O{}^{18}O\cdot \longrightarrow 2CH_3\cdot + {}^{46}CO_2 + {}^{34}O_2 \quad (7)$$

$$CH_3\cdot + {}^{32}O_2 \longrightarrow CH_3{}^{16}O{}^{16}O\cdot \quad (8)$$