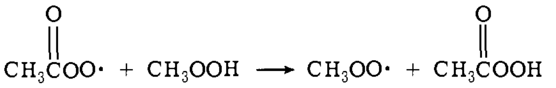
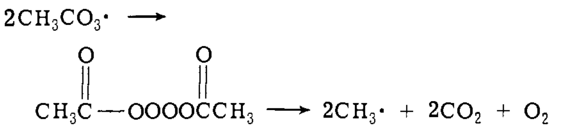
There is a virtual equilibrium between $CH_3OO\cdot$ and $AcOO\cdot$ through reaction 28. Therefore, even though acetaldehyde concentration is increased, the concentration of $CH_3OO\cdot$ might not be appreciably changed.



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}OO\cdot + CH_3OOH \longrightarrow CH_3OO\cdot + CH_3\overset{\overset{O}{\|}}{C}OOH} \quad (28)$$

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.



$$\mathrm{2CH_3CO_3\cdot \longrightarrow CH_3\overset{\overset{O}{\|}}{C}{-}OOO\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow 2CH_3\cdot + 2CO_2 + O_2} \quad (29)^{13}$$

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

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

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

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

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.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research for support of this project.

References and Notes

(1) Previous paper in this series in this issue.
(2) This work was supported by a grant from the Air Force Office of Scientific Research, AFOSR-69-1639.
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(13) The head-to-head interaction of acetoxy radicals has been further documented by an ESR study of these radicals at low temperature.[14]
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Autoxidation of Acetaldehyde. III. Oxygen-Labeling Studies[1,2]

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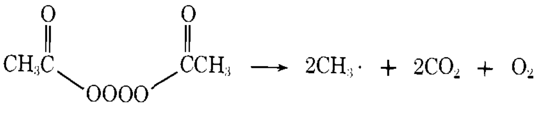
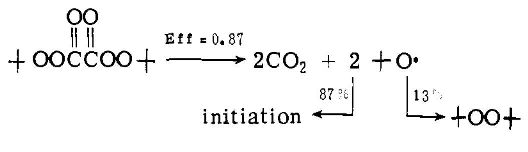
Abstract: The autoxidation of acetaldehyde in solution at 25° was studied using a mixture of 95% $^{32}O_2$ and 5% $^{36}O_2$. From a comparison of the rates of $^{34}O_2$, $^{32}O_2$, $^{44}CO_2$, and $^{46}CO_2$ evolution, the numbers of oxygen and carbon dioxide molecules evolved for each termination 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



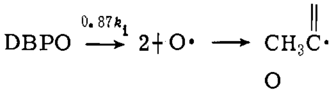
$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}{-}OOOO{-}\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow 2CH_3\cdot + 2CO_2 + O_2} \quad (1)$$

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

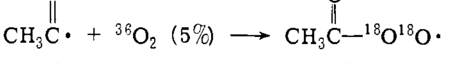


$$\mathrm{{+}OO\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}OO{+} \xrightarrow{Eff = 0.87} 2CO_2 + 2\,{+}O\cdot} \quad (3)$$

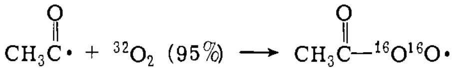
$$\mathrm{{+}O\cdot \xrightarrow{87\%} initiation; \qquad {+}O\cdot \xrightarrow{13\%} {+}OO{+}}$$



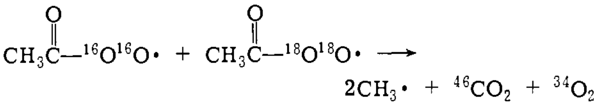
$$\mathrm{DBPO \xrightarrow{0.87k_1} 2{+}O\cdot \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\cdot} \quad (4)$$



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}\cdot + {}^{36}O_2\ (5\%) \longrightarrow CH_3\overset{\overset{O}{\|}}{C}{-}{}^{18}O^{18}O\cdot} \quad (5)$$



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}\cdot + {}^{32}O_2\ (95\%) \longrightarrow CH_3\overset{\overset{O}{\|}}{C}{-}{}^{16}O^{16}O\cdot} \quad (6)$$



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}{-}{}^{16}O^{16}O\cdot + CH_3\overset{\overset{O}{\|}}{C}{-}{}^{18}O^{18}O\cdot \longrightarrow 2CH_3\cdot + {}^{46}CO_2 + {}^{34}O_2} \quad (7)$$

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

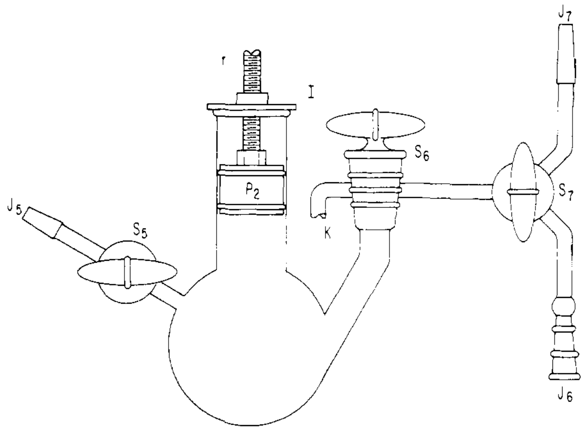


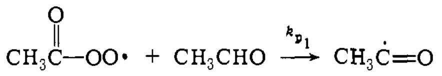
Figure 1. Reaction flask for oxygen-labeling studies of acetaldehyde autoxidation. The flask is a round-bottomed flask topped by a precision bore tube. A Teflon plunger, P_2, fitted with "O" rings and lightly greased affords a gas-tight seal when inserted into the tube. P_2 is attached to a threaded metal plate, I, and rod, r. P_2 is raised or lowered by rotating I around r. One full revolution of I changes the volume of R_2 by 1.0 cm^3. R_2 is also fitted with: two-way vacuum stopcocks, S_5 and S_6; 120° three-way vacuum stopcock, S_7; ₸ $^{10}/_{18}$ female joints, J_5 and J_6; ₸ $^{10}/_{18}$ male joint, J_7; outlet, K; magnetic stirring bar, M_2. R_2 is connected to a vacuum line at J_7, and to a mercury column through K, and a small piece of Tygon tubing. This mercury column is maintained very close to stopcock S_6 so that little of the gas goes into tube K during intermediate pressure measurements. The mercury column is also attached to the pressure measurement. By opening the stopcock to K, the pressure can be periodically checked to see that it doesn't fall below 0.5 atm. The volume of the flask with magnetic stirring bar and P_2 at the top of its travel is 147.4 ml.

$$CH_3\cdot + {}^{36}O_2 \longrightarrow CH_3{}^{18}O^{18}O\cdot \quad (9)$$

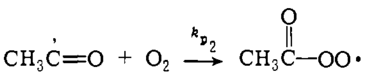
$$CH_3{}^{18}O^{18}O\cdot + CH_3{}^{16}O^{16}O\cdot \longrightarrow CH_3OH + CH_2O + {}^{34}O_2 \quad (10)$$

from both peroxy radicals but the amount of carbon dioxide from eq 1 separately from that of eq 3. That from acetylperoxy radicals will be labeled as $^{46}CO_2$.

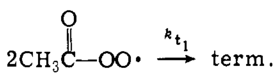
Although this system is capable of revealing more about termination processes than are similar studies in cumene autoxidation,[4] it is also subject to several difficulties associated with the high reactivity (long chain lengths) in aldehyde autoxidation.[2] At long chain lengths, the oxygen is consumed before evolution can be detected. Additionally, aldehyde autoxidations change kinetic behavior below about 200-Torr oxygen pressure so as to indicate a change in termination mechanism (eq 11–14).[6] Unlike cumene aut-



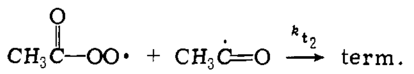
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OO\cdot + CH_3CHO \xrightarrow{k_{p_1}} CH_3\dot{C}{=}O \quad (11)$$



$$CH_3\dot{C}{=}O + O_2 \xrightarrow{k_{p_2}} CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OO\cdot \quad (12)$$



$$2CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OO\cdot \xrightarrow{k_{t_1}} \text{term.} \quad (13)$$



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OO\cdot + CH_3\dot{C}{=}O \xrightarrow{k_{t_2}} \text{term.} \quad (14)$$

oxidation, the abstraction process (k_{p_1}) is very fast, and therefore k_{p_2}/k_{p_1} is sufficiently small that, at low oxygen pressures, $CH_3\underset{\cdot}{C}O$ builds up to make the termination process (14) important.[6] Therefore a closed system such as that previously used for cumene (in which such termination mechanism change occurs below 1 Torr) cannot be used.

The problems were resolved in two ways. First, we took advantage of the observation in the previous paper in this issue[3] that added *tert*-butyl hydroperoxide at ~0.5 *M* decreases chain length but not carbon dioxide evolution rate, implying that this addition does not affect termination. We are therefore able to decrease the chain length to less than ten by chain transfer to *t*-BuOOH without changing the termination mechanism. Secondly, in order to keep oxygen pressure above 200 Torr in a closed system, we devised a variable-volume flask in which the volume can be decreased by known amounts as the reaction proceeds. This cannot be a simple buret, because the labeled oxygen must be homogeneous during the autoxidation.

Experimental Section

Reagents used in this work were described previously except for oxygen 36 (98.907%) which was purchased from the Isotope Department of the Weizman Institute of Science, Rehovoth, Israel.

Apparatus. Mass spectra were determined on a special spectrometer built by the cosmochemistry group at UCSD. This instrument has better peak height reproducibility than do most commercial instruments. The special variable-volume flask is shown in Figure 1.

Experimental Procedure. Referring to Figure 1, with S_5 closed, with S_6 and S_7 opened to the vacuum line, and, with the piston P_2 at 43 turns from the top position, the flask was evacuated through J_7. A 300-ml bulb containing approximately 5% $^{36}O_2$, 2% argon, and 93% normal oxygen was attached at J_6 and the space between the bulb and the flask evacuated. The gas was then admitted to the reaction flask and the stopcock S_6 turned to K for pressure measurement. At this point, the pressure was 633 Torr at 25°, and the gas volume was 104.1 ml (with the stirring bar in place), both measurements based upon prior calibrations of the flask and the transducer. A sample of gas (~0.5 ml) was removed for mass spectral analysis at this point. This sample is listed as sample 1 in the tables. The total amount of gas at zero time is 3.56×10^{-3} mol. The pressure in the flask was adjusted to 1 atm so that solutions could be added. From a 50.00-ml solution containing 103.5 mg of DBPO (0.0088 *M*) and 3.94 ml of purified *tert*-butyl hydroperoxide (0.78 *M*), 31.61 ml was injected into the flask in the following way. A calibrated syringe was fitted with a polyethylene needle which was designed to fit tightly at J_5. With the internal pressure set at 1 atm, the needle was quickly injected through S_5 and fitted at J_5. By raising the plunger P_2 as the solution was injected, 1 atm pressure could be maintained and, after the injection, the needle quickly withdrawn without gas leaking in or out. After placing the flask in a 25.0° bath equipped with magnetic stirrer, a single injection of 0.7171 ml (0.0128 *M*) of acetaldehyde was injected as described above. The pressure was 1 atm after this injection, and stirring was commenced.

Pressure was checked through K and adjusted to ~1 atm with P_2 as the reaction progressed, and additional samples were removed and analyzed by mass spectrometry as previously described. Relative peak heights, along with volume of the vapor phase at each point, are recorded in Table I. Initial conditions are listed in Table II.

Because the gases involved do not have the same sensitivity in mass spectroscopy or the same solubility as argon, corrections must be made for these factors in order to convert relative peak heights to quantities of each gas. Before this can be done, the $^{36}O_2$ peak must be corrected for a small ^{36}A peak as follows:

$$\text{Height}\,({}^{36}O_2) = H_{36} - 0.00334\,H_{40}$$

This correction amounts to about 1% reduction in mass 36 peak height. Argon affords a larger peak height for the same pressure than do the other gases. Thus the observed peak heights were multiplied by the sensitivity factors. (S_i) S_A (1.0), S_{O_2} (1.72), S_{N_2} (1.43), S_{CO_2} (1.22).[4] The solubilities (α) of oxygen and carbon dioxide in benzene at 25° are: α_{O_2} = 0.164 ml gas/ml solvent and α_{CO_2} = 2.22 ml gas/ml solvent, respectively,[4,7] and the total gas is then

$$N_{\text{total}} = N_{\text{vapor}}(1 + \alpha_i V_{\text{liq}}/V_{\text{vapor}}) \quad (15)$$

This correction varies with time, because the volume of the vapor varies (Table I). The number of moles of each gas (i) then becomes

Table I. Observed Mass Spectrometer Peak Heights (H_i) for the Autoxidation of CH_3CHO in the Presence of $^{36}O_2$

			$H_i \times 10^{-3}$						
Sample	Time, sec	V_{vapor}[a]	28	32	34	36	40	44	46
1	0		7.647	116.8	0.593	8.630	5.420	1.732	
2	43	100.1	9.763	83.00	0.400	5.680	3.680	2.336	
3	2670	97.1	13.10	105.0	0.640	7.480	5.020	5.494	
4	5460	94.1	11.52	93.50	0.610	6.560	4.920	4.564	
5	11003	91.1	12.97	122.2	1.020	8.430	6.440	10.277	0.349
6	22615	79.1	16.96	113.3	1.320	7.490	6.590	16.86	0.685
7	25840	79.1	14.90	99.50	1.260	6.580	6.130	17.17	0.705
8	34520	73.1	14.60	89.00	1.240	5.510	5.810	19.37	0.797
9	41890	70.1	14.92	82.50	1.400	5.070	5.960	22.43	0.921
10	49220	64.1	22.53	129.2	2.390	7.840	9.900	39.04	1.692
11	56315	58.1	17.53	86.70	1.610	5.050	7.210	30.54	1.254
12	63390	55.1	17.82	80.40	1.640	4.550	7.320	3.152	1.390
13	71850	52.1	18.97	78.10	1.660	4.210	7.790	35.60	1.582
14	85810	46.1	23.81	90.30	2.090	4.550	9.970	46.86	2.040
15	99490	39.3	22.54	75.90	2.030	3.720	9.710	45.75	1.898

[a] Calculated from the known reactor volume with P_2 at the top of its travel (147.4 ml), volume of solution, 1.0 ml × number of screw turns.

Table II. Conditions for Acetaldehyde Autoxidation at 25.0° in Benzene at Zero Time (43 sec)

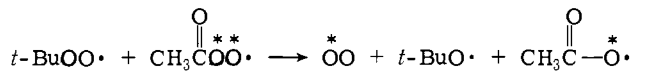
DBPO	2.78×10^{-4} mol
t-BuOOH	2.48×10^{-2} mol (0.78 M)
CH_3CHO	0.0128 mol
Total gas	3.56×10^{-3} mol
Argon	8.20×10^{-5} mol
Volume of reactor	132.4 ml
Volume of solution	32.3 ml
Volume of vapor phase	100.1

$$N_i = N_A\left(\frac{H_iS_i}{H_A}\,\frac{(V_{vapor} + \alpha_iV_{liq})}{V_{vapor}}\right) \qquad (16)$$

where H are peak heights, S_i are sensitivities, N_i are the number of moles of gas i in the reactor at the time of analysis, and N_A is the number of moles of argon in the flask initially (8.20×10^{-5} mol). (The small amounts of argon removed for analysis were not taken into account.) The total number of moles of each gas at each point, calculated in this way, is shown in Table III.

Results and Discussion

The data in Table III can be converted into rates of oxygen and carbon dioxide evolution by methods previously described. However, in the previous ^{18}O studies on cumene autoxidation, the only source of oxygen is the gaseous O_2. Consequently the atom fraction of ^{18}O remained constant. In the present study, the atom fraction of ^{18}O steadily decreases as the reaction proceeds, indicating oxygen evolution from unlabeled *tert*-butyl hydroperoxy radicals (eq 17 and 18). This result, although not predicted by the effect of *tert*-butyl hydroperoxide on CO_2 evolution,[3] affords additional information as we will show in the derivation below.



$$t\text{-BuOO}\cdot + CH_3\overset{O}{\overset{\|}{C}}\overset{*}{O}\overset{*}{O}\cdot \longrightarrow \overset{*}{O}O + t\text{-BuO}\cdot + CH_3\overset{O}{\overset{\|}{C}}-\overset{*}{O}\cdot$$

or (17)

$$t\text{-BuOO}\cdot + CH_3\overset{*}{O}\overset{*}{O}\cdot \longrightarrow \overset{*}{O}O + t\text{-BuOH} + CH_2\overset{*}{O} \qquad (18)$$

Following the previous derivations, we will make the definitions.

β = molecules of oxygen evolved per chain terminating encounter of two radicals.

x = moles of $^{32}O_2$ in the reactor, y = moles of $^{34}O_2$ in the reactor, z = moles of $^{36}O_2$ in the reactor. $w = x + y + z$.

q = moles of O_2 ($^{32}O_2$ or $^{34}O_2$) derived from reactions 17 or 18, each molecule containing one atom of oxygen from the unlabeled hydroperoxide.

$M_j = j/w$ where j is x, y, z, q and M_j the mole fraction of species j.

$a_t = M_z + \frac{1}{2}M_y$, the atom fraction of ^{18}O at time t.

f_y = statistical fraction of generated O_2 which is $^{34}O_2$, assuming all reactions involve only AcOO· and CH_3OO· radicals. $f_y = 2(1 - a)$, $f_z = a^2$, $f_q = 1$ (for reactions 17 and 18).

C_i = rate of consumption of species i by the reaction R· + $O_2 \rightarrow$ ROO·. $C_w = \Sigma C_i$.

G_i = rate of generation of species i due to a defined encounter between ROO·. $G_w = \Sigma G_i$.

$b = C_w - G_w$ = observed oxygen consumption in mol/sec = $-\mathrm{d}w/\mathrm{d}t$.

$G_W = G_w' + G_w''$, G_w' = generation from *tert*-butylperoxy radicals, G_w'' = generation from all other sources (eq 7 and 10).

Following the derivation of Bartlett[4] for $^{34}O_2$, we let

$$\mathrm{d}y/\mathrm{d}t = G_y - C_y = G_wf_y - C_wM_y \qquad (19)$$

and substitute $y = wM_y$, $\mathrm{d}z = w\mathrm{d}M_y + M_y\mathrm{d}w$, $-\mathrm{d}t = \mathrm{d}w/b$ to obtain (if $G_w = G_w''$)

$$b(wM_y + M_y\mathrm{d}w)/ - \mathrm{d}w = G_wf_y - (G_w + b)M_y \qquad (20)$$

$$(bwM_y/\mathrm{d}w) - bM_y = G_wf_y - G_wM_y - bM_y \qquad (21)$$

Integration gives (if $G_w = G_w''$)

$$\log (f_y - M_y) = (G_w''/b) \log w + \text{const} \qquad (22)$$

A similar derivation for oxygen generation exclusively based upon reactions 17 and 18 yields

$$\log (f_q - M_q) = (G_w'/b) \log w + \text{const}' \qquad (23)$$

For $^{36}O_2$ changes, the same derivation gives

$$\log z = [(G_w + 1)/b] \log w + \text{const}'' \qquad (24)$$

The mole fractions of $^{36}O_2$, $^{34}O_2$, $^{34}O_2$ and q, the O_2 from t-BuOOH, are listed in Table IV along with the atom fraction of ^{18}O at each point. M_q is obtained from the increased $^{32}O_2$ as measured by decrease in a (eq 25). The derived

$$M_q \text{ (at } t) = \frac{a_0 - a_t}{a_0} \qquad (25)$$

quantities to be used in plotting eq 22, 23, and 24 are listed in Table V. Equations 22 and 24 are plotted in Figures 2 and 3.

A plot of total oxygen (w) vs. time is shown in Figure 4. From the "y slope" = 0.40 and z slope = 1.41, we might conclude that $G_w = b \times 0.41 = 8.6 \times 10^{-9}$ M sec^{-1}. However, a simple plot of q vs. time (not shown) reveals that at least 2.4×10^{-9} M sec^{-1} of oxygen arises from interactions of t-BuOO·. A plot of eq 23 (slope 0.16) suggests that at least 3×10^{-9} M sec^{-1} oxygen arises from this source. Therefore, this reaction cannot be ignored. The applications

Table III. Corrected Moles of Gases for the Autoxidation of CH_3CHO in the Presence of $^{36}O_2$

	Moles × 10^4						
Time, sec	Mass 28	$^{32}O_2$ (x)	$^{34}O_2$ (y)	$^{36}O_2$ (z)	w^a	$^{44}CO_2$	$^{46}CO_2$
0	1.65	30.37	0.1543	2.240	32.77	0.3192	
43	3.10	33.44	0.1611	2.284	35.89	1.0788	
2670	3.04	31.22	0.2367	2.209	33.67	1.884	
5460	2.74	28.27	0.1845	1.979	30.44	1.619	
11083	2.35	28.28	0.2361	1.947	30.47	2.919	0.0958
22615	3.00	25.84	0.3010	1.704	27.85	5.021	0,1960
25840	2.84	24.38	0.3088	1.608	26.30	5.662	0.1974
34520	2.93	23.06	0.3222	1.427	24.88	6.801	0.1689
41890	2.92	20.96	0.3557	1.283	22.60	7.832	0.3089
49220	2.66	19.89	0.3680	1.202	21.46	8.614	0.3578
56315	2.84	18.47	0.3431	1.073	19.89	9.727	0.3838
63390	2.84	16.94	0.3456	0.9537	18.24	10.21	0.4315
71850	2.84	15.54	0.3303	0.8326	16.71	11.19	0.4762
85810	2.78	14.19	0.3285	0.7109	15.23	12.36	0.5158
99490	2,78	12.47	0.3335	0.6061	13.41	13.62	0.05443

[a] $w = x + y + z$.

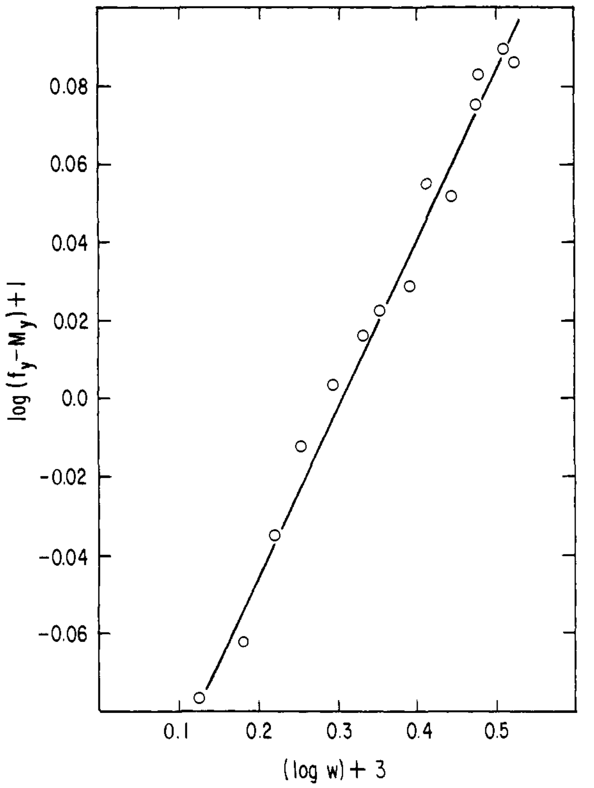


Figure 2. Plot of log $(f_y - M_y)$ vs. log w where $f_y = 2(1 - a)$ and it is assumed that only reactions 7 and 10 lead to oxygen evolution. Slope = 0.41.

Table IV. Oxygen Mole Fractions $(M_i)^a$ and Atom Fraction of ^{18}O (a) for the Autoxidation of CH_3CHO in the Presence of $^{36}O_2$

Time, sec	$M_x \times 10^2$	$M_y \times 10^2$	$M_z \times 10^2$	$M_q \times 10^{2\,b}$	$a \times 10^2$
0	92.69	0.471	6.835		7.071
43	93.18	0.449	6.346		6.813
2670	92.73	0.703	6.560		6.912
5460	92.89	0.606	6.502	0.117	6.805
11083	92.83	0.775	6.388	0.56	6.775
22615	92.79	1.081	6.119	2.74	6.660
25840	92.71	1.174	6.112	1.61	6.699
34520	92.96	1.295	5.736	4.25	6.384
41890	92.74	1.574	5.677	5.1	6.464
49220	92.68	1.715	5.601	5.2	6.459
56315	92.88	1.725	5.394	8.2	6.257
63390	92.87	1.895	5.229	6.2	6.177
71850	93.03	1.977	4.984	12.3	5.973
85810	93.18	2.157	4.661	15.7	5.740
99490	92.99	2.487	4.518	15.4	5.762

[a] Analysis of gas mixture before it was admitted to the reaction flask. [b] Based upon the 43 sec point taken as a zero time composition.

Table V. Miscellaneous Values Calculated for the Autoxidation of CH_3CHO in the Presence of $^{36}O_2$

Time, sec	f_y	Log $(f_y - M_y)$ + 1	Log $(f_q - M_q)$ + 1	Log z + 5	Log w + 3
0	0.1314	0.1028		1.350	0.5155
43	0.1269	0.08808		1.359	0.5550
2670	0.1286	0.08513		1.344	0.5271
5460	0.1268	0.08199	0.968	1.296	0.4834
11083	0.1263	0.07397	0.967	1.289	0.4824
22615	0.1232	0.0510	0.959	1.231	0.4447
25840	0.1250	0.05409	0.962	1.206	0.4199
34520	0.1195	0.02767	0.952	1.154	0.3959
41890	0.1209	0.02194	0.945	1.108	0.3541
49220	0.1208	0.01572	0.945	1.079	0.3314
56315	0.1173	0.00260	0.932	1.031	0.2986
63390	0.1159	0.01341	0.942	0.9794	0.2610
71850	0.1123	0.03360	0.912	0.9204	0.2229
85810	0.1082	0.06227	0.895	0.8518	0.1827
99490	0.1086	0.07711	0.896	0.7825	0.1274

of reactions 22, 23, and 24 are therefore incorrect as used in Figures 2 and 3, because $C_w \neq G_w + b$ for either the assumption that G_w = that from eq 7 and 10 or that from eq 17 and 18. We must correct f_y, f_z, and f_q for the amounts of pathways 7 and 10 compared with those of 17 and 18.

Let δ = fraction of O_2 evolution resulting from reactions 7 and 10 and $1 - \delta$ the fraction from 17 and 18. Then the corrected f_y and f_q which were previously taken as $2a(1 - a)$ and 1.0, respectively, become

$$f_y' = \delta 2a(1 - a) + (1 - \delta)a$$

and

$$f_q' = 1 - \delta$$

Thus the corrected eq 22 is

$$\log \{[2a(1 - a) + (1 - \delta)a] - M_y\} = (G_w/b) \log w + \text{const} \quad (26)$$

and eq 23 becomes

$$\log (1 - \delta - M_q) = (G_w/b) \log w + \text{const} \quad (27)$$

Plots of eq 26 and 27 must have the same slope, G_w/b. The value of δ which gives the best match of these slopes is 0.6. Plots of eq 25 and 26 are shown in Figure 5, using $\delta = 0.6$. The slopes of these rather inaccurate plots are about 0.5, and this indicates that the corrected $G_w^{corr} = 0.5\, b \cong 10 \times 10^{-9}$ M sec^{-1} which is somewhat higher than the uncor-

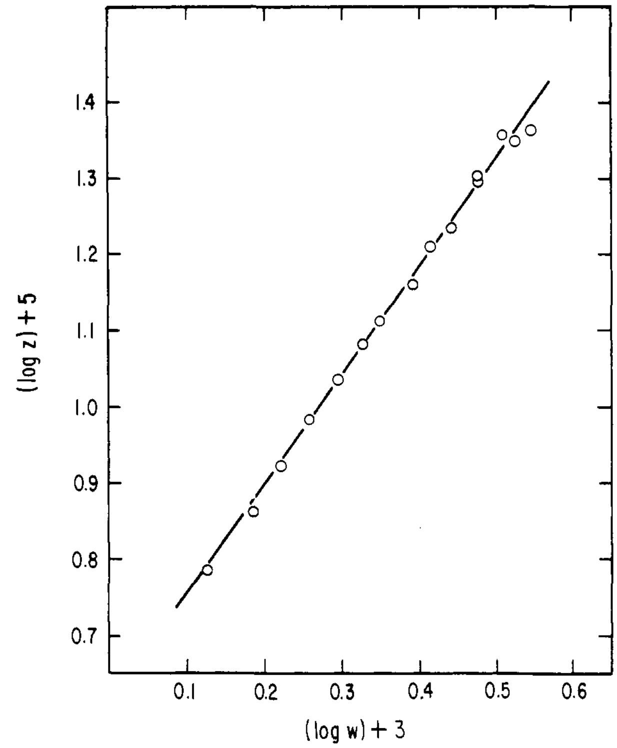


Figure 3. Plot of log z vs. log w assuming that all evolved oxygen comes from reactions 7 and 10. Slope = 1.41.

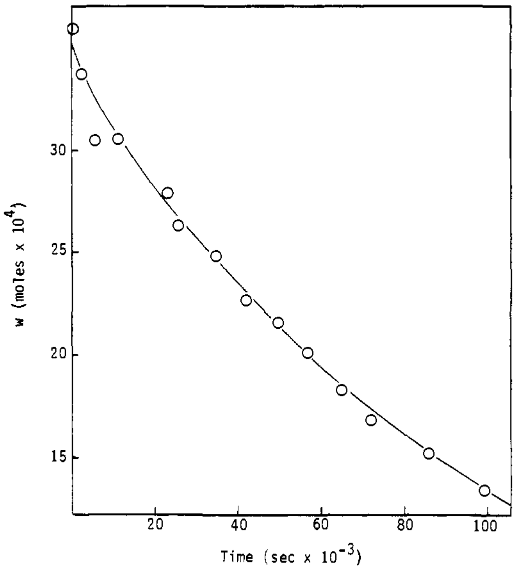


Figure 4. Rate of total oxygen consumption dw/dt. Average slope $\cong$ 2.8×10^{-8} M sec^{-1}.

rected G_w. From the value of $\delta = 0.6$, we conclude that $G_w''(7 \text{ and } 10) = 6 \times 10^{-9}$ M sec^{-1} and that from $\dashv$ OOH $G_w'(17 \text{ and } 18) = 4 \times 10^{-9}$ M sec^{-1}.

Because the reaction was run longer than 1 half-life of initiator decomposition ($t_{1/2} = 4.9 \times 10^4$ sec), R_i changed as did the rate of oxidation $b = dw/dt$ shown in Figure 4. Because the number of oxygens evolved per terminating step is given by

$$\beta = G_w/2R_i = \frac{y \text{ slope} \times b}{2e(1.41 \times 10^{-5})[\text{DBPO}]} \tag{28}$$

we should calculate β at each point. But both b and R_i decrease with time, and therefore the value of β remains approximately constant. For a representative value of β, we take the average value of $b = 2 \times 10^{-8}$ M sec^{-1}, and $R_i/2$

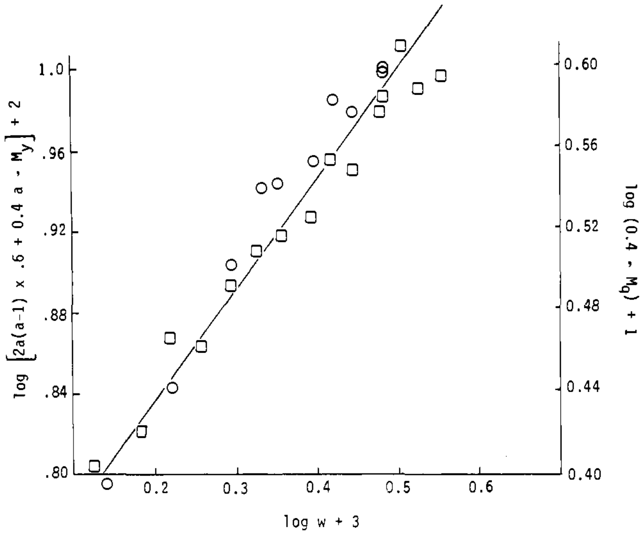


Figure 5. Plots of corrected log $(f_y' - M_y)$ (□) and log $(f_q' - M_q)$ (○) vs. log w for 40% oxygen production from reaction 17 or 18.

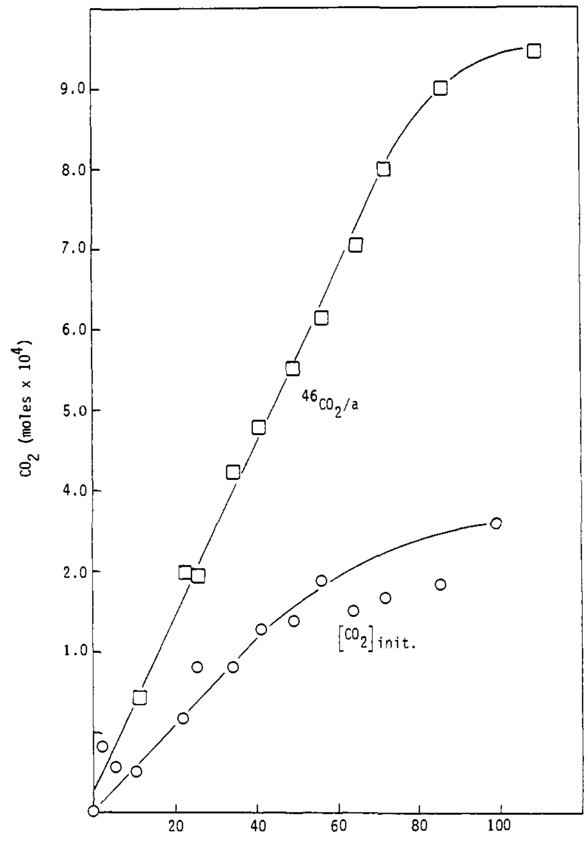


Figure 6. Plots $[CO_2]$ vs. time. ○, $[CO_2]_{init} = {}^{44}CO_2 - {}^{46}CO_2/a$. Slope $= 4.5 \times 10^{-9}$ M sec^{-1}. □, $^{46}CO_2/a$. Slope $= 10.6 \times 10^{-9}$ M sec^{-1}.

is about 3×10^{-9} M sec^{-1}. Then $\beta \cong 3$ per pair and $G_w \cong 1 \times 10^{-8}$ M sec^{-1}. Approximately one of these three comes from reactions 17 and/or 18 and two from other interactions.[9]

The carbon dioxide evolution from acetylperoxy radicals must include a fraction a (the fraction ^{18}O) of $^{46}CO_2$. Therefore the rate of CO_2 generation from this source is obtained by dividing the rate of $^{46}CO_2$ evolution by a. Plots of $^{46}CO_2/a$ and $^{44}CO_2 + {}^{46}CO_2 - {}^{46}CO_2/a = [CO_2]_{init}$, both obtained from Tables III and IV, vs. time are shown in Figure 6.

$$\left(\frac{\mathrm{d}[\mathrm{CO_2}]}{\mathrm{d}t}\right)_{\text{from } \mathrm{CH_3\overset{O}{\overset{\|}{C}}OO\cdot}} = \left(\frac{\mathrm{d}[^{46}\mathrm{CO_2}]}{\mathrm{d}t}\Big/ a\right) = 11 \times 10^{-9}\ M\ \mathrm{sec}^{-1} \quad (29)$$

then

$$\left(\frac{\mathrm{d}[\mathrm{CO_2}]}{\mathrm{d}t}\right)_{\text{from DBPO}} = \left(\frac{\mathrm{d}[\mathrm{CO_2}]}{\mathrm{d}t}\right)_{\text{total}} \left(\frac{\mathrm{d}[\mathrm{CO_2}]}{\mathrm{d}t}\right)_{\mathrm{CH_3\overset{O}{\overset{\|}{C}}OO\cdot}} \quad (30)$$

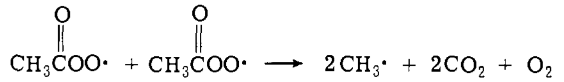
From these rates, the number of CO_2 molecules per termination step is

$$\mathrm{CO_2/term.} = (\mathrm{d}[\mathrm{CO_2}]/\mathrm{d}t)_{\mathrm{CH_3\overset{O}{\overset{\|}{C}}OO\cdot}}/0.87(\mathrm{d}[\mathrm{CO_2}]/\mathrm{d}t)_{\text{init}} = 2.5/\text{chain} = 5.0/\text{pair}$$

or, based upon calculated initiation rates

$$\mathrm{CO_2/term\cdot} = \frac{(\mathrm{d}[\mathrm{CO_2}]/\mathrm{d}t)_{\mathrm{CH_3\overset{O}{\overset{\|}{C}}OO\cdot}}}{2ek_1[\mathrm{DBPO}]} \cong 3 \text{ per chain or } 6 \text{ per pair}$$

Therefore, the interaction of acetylperoxy radicals gives about 2.5 O_2 and 5 CO_2 in 2½ bimolecular interactions before termination, and about one more O_2 comes from *t*-BuOO· radicals, either through termination or self-reaction of *t*-BuOO· radicals. This would be explained by the reactions 31–34. These results corroborate the oxygen evolution



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}OO\cdot + CH_3\overset{O}{\overset{\|}{C}}OO\cdot \longrightarrow 2CH_3\cdot + 2CO_2 + O_2} \quad (31)$$

$$\mathrm{CH_3\cdot + O_2 \longrightarrow CH_3OO\cdot} \quad (32)$$

$$\mathrm{CH_3OO\cdot} + t\text{-}\mathrm{BuOO\cdot \longrightarrow CH_2O + O_2} + t\text{-}\mathrm{BuOH} \quad (33)$$

$$2t\text{-}\mathrm{BuOO\cdot} \longrightarrow 2t\text{-}\mathrm{BuO\cdot + O_2} \quad (34)$$

for acetylperoxy[7] and secondary alkylperoxy[8] radicals previously reported. In the absence of *t*-BuOOH, reaction 33 would be replaced by an interaction of methylperoxy radicals with themselves or with acetylperoxy radicals.

We conclude that all evidence presented in these three papers points to nonterminating interactions of acylperoxy radicals followed by termination involving the alkyl radicals from decarboxylation. This leaves the rapid termination of benzaldehyde[6] autoxidation, in which decarboxylation is very slow, a mystery to be investigated.

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References and Notes

(1) Supported by the Air Force Office of Scientific Research, Grant No. AFOSR-69-1639.

(2) A previous paper (Acetaldehyde Autoxidation. I.) in this issue.

(3) Previous paper (Acetaldehyde Autoxidation. II.) in this issue.

(4) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963).

(5) P. D. Bartlett and T. G. Traylor, unpublished work.

(6) J. F. Griffiths and G. Skirrow in "Oxidation and Combustion Reviews", Vol. 3, C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1968, p 47.

(7) J. E. Bennett and J. A. Howard, *J. Am. Chem. Soc.*, **95**, 4008 (1973).

(8) P. D. Bartlett and T. G. Traylor (unpublished), using the same mass spectrometric technique as was used in cumene autoxidation, showed that termination of the autoxidations of tetralin gave about 0.8 O_2 per termination step independent of chain length. Similar results were observed for the autoxidations of 1,3-dioxalane and ethylbenzene and the oxidation of methyl radicals.

(9) If we had assumed that all the extra ^{16}O had come from self-reactions of *t*-BuOO· radicals resulting in an M_q', then $M_q' = \frac{1}{2}M_q$ and, in a plot like that in Figure 5, about 20% rather than 40% of evolved oxygen would arise from interactions of *t*-BuOO· radicals. This result would not change the conclusions of this paper.

Three-Electron Oxidations. X. Cooxidation of Isopropyl Alcohol and Glycolic Acid[1,2]

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Abstract: The chromic acid oxidation of a mixture of glycolic acid and isopropyl alcohol is a fast cooxidation process yielding acetone and gloxylic acid in an approximately 2:1 ratio. The mechanism consists in the formation of a termolecular complex of chromium(VI) with glycolic acid and isopropyl alcohol, which decomposes in a rate-limiting step in a three-electron oxidation–reduction process to a molecule of acetone, chromium(III), and a free radical intermediate $HO\dot{C}H\dot{C}O_2H$ which is subsequently oxidized to glyoxylic acid. The substantial isotope effect observed for both substrates ($HOCH_2CO_2H$–$(CH_3)_2CDOH$, 6.0; $HOCD_2CO_2H$–$(CH_3)_2CHOH$, 5.8; $HOCD_2CO_2H$–$(CH_3)_2CDOH$, 34.4) provides clear evidence for the synchronous breaking of two different C–H bonds in the rate-limiting step. It also represents convincing proof for the proposed three-electron oxidation mechanism.

Chromic acid reacts with two-component systems containing oxalic acid together with a primary or secondary alcohol,[3,4] malachite green,[5] or indigo,[6] by several orders of magnitude faster than with either oxalic acid or the other component alone. A number of other bi- and polyfunctional compounds exhibit a similar effect as oxalic acid.[7,8]

In several cases it has been conclusively demonstrated that this rapid reaction is a cooxidation, in which both substrates are oxidized.[3-5,8] On the other hand, rapid oxidations of two-component systems in which only one of them is oxidized while the other acts as a catalyst have also been found: oxalic acid acts as an efficient catalyst in the oxidation of iodide[9] and of thiocyanate;[10] picolinic acid greatly accelerates the oxidation of alcohols.[11] At this point the amount of information on cooxidation and on catalysis in chromic acid oxidations is insufficient to permit the drawing of more general conclusions about the conditions necessary for either of these two processes to take place. Further study of both reaction types is therefore needed.

In this paper we wish to present the results of a detailed