vacuo, and the residue was extracted with 40 ml of warm benzene. There remained 1.1 g of unreacted ferrocenecarboxylic acid. Cooling of the benzene extract at 0° for several hours gave 4.0 g (40.0%) of *sym*-tetraphenyldiferrocenoyloxyditin as bronze-colored crystals, mp 180–182°. Recrystallization from ethyl acetate did not raise the melting point.

Diphenyltin Diferrocenoate. A.—Triphenyltin ferrocenoate, mp 120–122° (0.587 g, 0.001 mole), was slurried with 40 ml of petroleum ether and poured onto 40 g of silica gel. The column was eluted with 500 ml of petroleum ether, which, on evaporation, gave a small amount (*ca.* 0.1 g) of unchanged triphenyltin ferrocenoate, mp 120–122°. Further elution with 1000 ml of methylene chloride gave, after evaporation, 0.46 g of solid, which, after recrystallization from benzene–petroleum ether, afforded 0.34 g of diphenyltin diferrocenoate: mp 240–241°, no depression on admixture with samples prepared by methods B and C below; $\bar{\nu}_{max}^{KBr}$ 1517, 1486, 1471 (COO) cm⁻¹.

Anal. Calcd for $C_{34}H_{28}Fe_2O_4Sn$: C, 55.86; H, 3.86. Found: C, 56.07; H, 3.81.

B.—A mixture of sodium ferrocenoate (1.26 g, 0.005 mole), diphenyltin dichloride (0.86 g, 0.0025 mole), and 95% ethanol (25 ml) was refluxed for 24 hr, the solvent was removed *in vacuo*, and the residue was extracted twice with 100-ml portions of benzene–methylene chloride (1:1). Concentration of the extract to 20 ml gave 0.55 g (30.2%) of diphenyltin diferrocenoate, mp 241–243°.

C.—A mixture of ferrocenecarboxylic acid (0.23 g, 0.001 mole), triphenyltin ferrocenoate (0.578 g, 0.001 mole), and 95% ethanol (10 ml) was refluxed for 24 hr, cooled, and filtered to give 0.6 g of orange solid, mp 236–238°. Recrystallization from benzene–methylene chloride gave 0.5 g (68.5%) of diphenyltin diferrocenoate, mp 241–243°.

Hydrolysis of Triphenyltin Esters on Woelm Alumina. A.—Triphenyltin ferrocenoate (0.578 g, 0.001 mole) was slurried with 40 ml of petroleum ether and poured onto 40 g of Woelm neutral alumina (activity II–III). The column was eluted first with 1000 ml of petroleum ether and then with 500 ml of methylene chloride. Evaporation of the methylene chloride *in vacuo* left 0.350 g of solid, which afforded, after recrystallization from 95% ethanol, 0.25 g (70.0%) of bis(triphenyltin) oxide, mp 119–121°. A mixture melting point with an authentic sample was undepressed. The infrared spectrum was superimposable on that of an authentic sample.

Further elution with 10% aqueous ammonium hydroxide gave 250 mg of solid, which was dissolved in water and acidified with concentrated hydrochloric acid to give, after filtration, 0.200 g (86.9%) of ferrocenecarboxylic acid, mp 218–222°, no depression on admixture with an authentic sample.

B.—Following the procedure described in A above, there was obtained from 1.0 g (0.0022 mole) of triphenyltin pyrrole-2-carboxylate, 0.5 g (70.0%) of bis(triphenyltin) oxide, and 0.17 g (70.0%) of pyrrole-2-carboxylic acid.

# Mechanism of Ozonation Reactions. II. Aldehydes

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Aldehydes react with ozone by an electrophilic mechanism (ρ values -1.1 to -0.6) in ethyl acetate and in pyridine. The deuterium isotope effect on ozone-catalyzed autoxidation, a reaction involving radical abstraction of hydrogen, was $k_H/k_D = 7.8$ at 0°, while decreasing the amount of autoxidation by decreasing the amount of oxygen or selectively destroying peroxidic material with pyridine gave k_H/k_D values from 1.2 to 2.0. It is suggested that initial attack of ozone on aldehydes involves either the direct insertion of ozone into the carbon–hydrogen σ bond, as postulated by White and Bailey, or the formation of a five-membered ring which then rearranges to the same intermediate.

White and Bailey have recently reinvestigated the reaction of ozone with aldehydes.[2] Their work showed that, contrary to previous reports,[3] per acids are formed when aldehydes are ozonized with either ozone–oxygen or ozone–nitrogen streams. They also determined, by product analysis after 1 mole equiv. of ozone had been passed through three *para*-substituted benzaldehydes, the reactivity sequence p-MeO > p-H > p-NO₂ and concluded that initial attack of ozone on aldehydes is not nucleophilic. This fact, along with other information from their rather complete product analysis, led to the proposal of I as the initial product of ozonation. I might then decompose to give various radicals which would catalyze the autoxidation of the aldehyde.

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-O-O-O-H$$
$$I$$
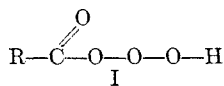
Since Walling and McElhill[4] have shown the same reactivity sequence (*i.e.*, p-MeO > p-H > p-CN)

for the free-radical catalyzed autoxidation of aldehydes, some caution must be exercised in interpreting Bailey's reactivity sequence.

Slomp and Johnson[5] have argued that the presence of pyridine in a solvent mixture greatly decreases the rate of the electrophilic addition of ozone to alkenes and have suggested that nucleophilic attack of ozone on aldehydes may take place when fairly large amounts of pyridine are present. They also note that, in the ozonation of alkenes, much less titratable peroxide is present when relatively small amounts of pyridine are present, while Bailey[6] reports the use of pyridine as a reducing agent for the decomposition of peroxides formed in the ozonation of pyrene. Supposedly, the product of these reductions is pyridine oxide, and Slomp gathered some evidence for its presence in his publication.[5]

We have been interested in the mechanism of the ozonation of aldehydes in particular and relative rates of ozonations in general for some time.[7] This paper reports our work on the relative rate method for the ozonation of various substituted benzaldehydes in ethyl acetate and in pyridine. The deuterium isotope effect k_H/k_D is also reported and discussed for benzalde-

(1) To whom requests for reprints should be addressed: Chemistry Department, University of Montana, Missoula, Mont.

(2) H. M. White and P. S. Bailey, *J. Org. Chem.* **30**, 3037 (1965). This paper includes references for most of the other work done on the aldehyde ozonation mechanism.

(3) E. Briner, Advances in Chemistry Series, No. 21, American Chemical Society, Washington, D. C., 1959, p. 184, and earlier references therein.

(4) C. Walling and E. A. McElhill, *J. Am. Chem. Soc.*, **73**, 2927 (1951).

(5) G. Slomp and J. L. Johnson, *ibid.*, **80**, 915 (1958).

(6) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(7) R. E. Erickson and T. Myszkiewicz, *J. Org. Chem.*, **30**, 4326 (1965).
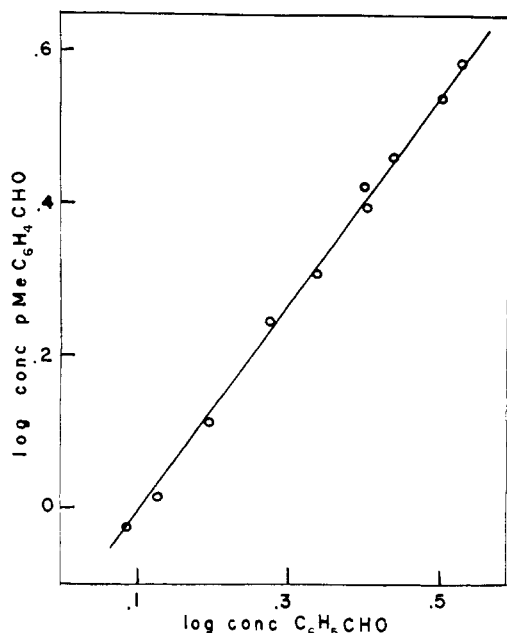
Figure 1.—Log concentration of p-tolualdehyde $vs.$ log concentration of benzaldehyde for competitive ozonation with ozone nitrogen in ethyl acetate. The slope of the line gives a ratio of rate constants of 1.36. Concentrations are relative rather than absolute.

hyde and benzaldehyde-formyl-d, under various ozonation conditions.

Experimental Section

Materials.—All aldehydes were reagent grade and were distilled or recrystallized before use. Solvents were pure and anhydrous. Benzaldehyde-formyl-d was prepared by the method of Wiberg as modified by Hauser.[8]

Ozonations.—The ozonations were carried out using a Welsbach T-23 ozonator and ozonation flasks of the type described by Bailey. The ozonator was allowed to run for at least 0.5 hr. to assure a reasonably constant ozone content for all ozone-oxygen runs, while the ozone–nitrogen work made use of ozone adsorbed on silica gel as described by Cook and co-workers.[9] For the relative rates determined by the competitive method, equal molar quantities (~0.05 mole for ethyl acetate work and ~0.015 mole for pyridine) of benzaldehyde and an appropriately substituted benzaldehyde were dissolved along with an internal standard (nitrobenzene, p-nitrotoluene, m-nitrotoluene, or o-nitrotoluene) in 75 to 100 ml. of solvent. Ozonations were carried out at 0° and samples (0.2 to 0.5 ml.) were withdrawn periodically. For the ozonations in ethyl acetate, this sample was immediately treated with 1 N potassium hydroxide. The purpose of this treatment was to remove acids which sometimes interfered with the gas chromatograms.[10] Samples were injected into the gas chromatograph within 1 min. of removal from the ozonation vessel.

For the pseudo-first-order method, only one aldehyde and an internal standard were employed, but the rest of the technique was the same. Since the assumption of constant ozone concentration is inherent in the pseudo-first-order method, the data reported were all obtained the same day, using the same flow and ozonator voltage. Previous work[11] has shown that our ozonator puts out relatively constant ($\pm5\%$) ozone over a 5-hr. period.

For the competitive ozonations in pyridine, samples were immediately injected into the gas chromatograph without further treatment.

(8) (a) K. B. Wiberg, $J.$ $Am.$ $Chem.$ $Soc.,$ **76**, 5371 (1954); (b) C. R. Hauser, P. J. Hamrick, Jr., and A. T. Stewart, $J.$ $Org.$ $Chem.,$ **21**, 260 (1956).

(9) (a) P. S. Bailey, $J.$ $Am.$ $Chem.$ $Soc.,$ **78**, 3811 (1956); (b) G. A. Cook, A. D. Kiffer, C. V. Klump, A. H. Malik, and L. A. Spence, ref. 3, p. 44.

(10) Runs were made without the basic work-up procedure, and slopes identical with those reported in this paper were obtained for the first 25–35% of the reaction. After that, the benzoic acid peak interfered severely.

(11) T. Myszkiewicz, M.S. Thesis, Canisius College, 1964.

The ozonations of benzaldehyde and benzaldehyde-formyl-d required slightly different work-up procedures. Here three different solvents, carbon tetrachloride, ethyl acetate, and pyridine, were employed. Work-up procedures for the carbon tetrachloride and ethyl acetate work involved washing successively with potassium iodide, sodium thiosulfate, and sodium hydroxide solutions. Aliquots for the ozonations in pyridine were added to 1 ml. of carbon tetrachloride, which was then washed with 6 N HCl and dilute sodium hydroxide solutions.

The stoichiometry of the ozonation reactions under the three sets of conditions used for the linear free energy (l.f.e.) plots was as follows: ozone–oxygen in ethyl acetate, 0.35 to 0.5 mole of ozone/mole of aldehyde oxidized; ozone–nitrogen in ethyl acetate, >1 mole of ozone/mole of aldehyde oxidized; and ozone–oxygen in pyridine, 4 moles of ozone/mole of aldehyde oxidized.

In all runs the ozonations were not quantitative; that is, some ozone escaped through the ozonation vessel into the potassium iodide trap.

In a separate experiment, pyridine N-oxide was ozonized in ethyl acetate with an ozone–oxygen stream, samples were withdrawn periodically, and their n.m.r. spectra were recorded. The characteristic absorption peaks of the pyridine N-oxide disappeared, showing that it had reacted with ozone. This indicates that at least part of the 4:1 ozone:aldehyde ratio found in pyridine ozonations may be due to pyridine N-oxide ozonation and may indicate why Slomp and Johnson were unable to isolate pyridine oxide in their work.[5]

Analytical Method.—All analytical data used for the linear free-energy plots were obtained by vapor phase chromatography on a Perkin-Elmer 154B vapor fractometer with external Variac-controlled injection-block temperature. The column used was 40% silicone grease (Dow–Corning high vacuum) on 30–60 mesh Chromasorb P, described by Carson and Miller.[12]

Typical gas chromatographic conditions were oven temperature, 175°; flow, 400 cc./min.; sample size, 2–10 μl.; and recorder range, 1. Under these conditions, all peaks were sharp with essentially no tailing. Generally, peak heights were measured and taken as proportional to concentration after correction by use of the internal standard. In several cases peak areas were used (determined by an Ott planimeter) with no significant change in results. For each kinetic run, between 6 and 12 injections were made. The number of samples per run was often lower with the ozone–oxygen work because the reactions were (as much as 90%) over within 30 min. Relatively long retention times for some of the high-boiling aldehydes such as p-anisaldehyde (5 min.) also decreased the number of samplings in some cases.

Figure 1 shows a typical plot of log concentration $vs.$ log concentration for a competitive run with ozone–nitrogen in ethyl acetate, while Figure 2 shows a log concentration $vs.$ time plot for three typical pseudo-first-order plots. The log concentration $vs.$ log concentration plots occasionally showed greater scatter than the one shown. p-Bromobenzaldehyde in particular, gave poorer plots, perhaps because of its relatively long retention time. Some data were obtained using m-nitrobenzaldehyde and p-nitrobenzaldehyde, but the reproducibility was poor. The rate of ozonation of p-cyanobenzaldehyde increased with time, probably because of rapid reaction with perbenzoate ion in the basic work-up procedure.

Deuterium isotope effect data were obtained using n.m.r (Varian A-60) spectroscopy and a pseudo-first-order method. An internal standard was used for the ozonations (1,1,2,2-tetrachloroethane, 5.95 p.p.m., for the ethyl acetate work and 2-octanone, 2.05 p.p.m., for the pyridine work), and the aromatic region (7.85 p.p.m.) was integrated and standardized to absolute concentrations. The aldehydic proton could also be used for the benzaldehyde work. Figure 3 shows a typical plot of log concentration $vs.$ time for benzaldehyde and benzaldehyde-formyl-d with ozone–oxygen.

This method was not applicable to the study of ozonations involving ozone–nitrogen streams, since ozone flow is not constant in this method. The competitive method was attempted, but rather large deviations were observed in the relative rate plots, probably because the method (subtraction of aldehydic proton area from aromatic area to give the benzaldehyde-formyl-d area) was extremely dependent on the relatively small aldehydic proton area. The data for Figure 4 were obtained by running two simultaneous ozonations from one ozone–nitrogen

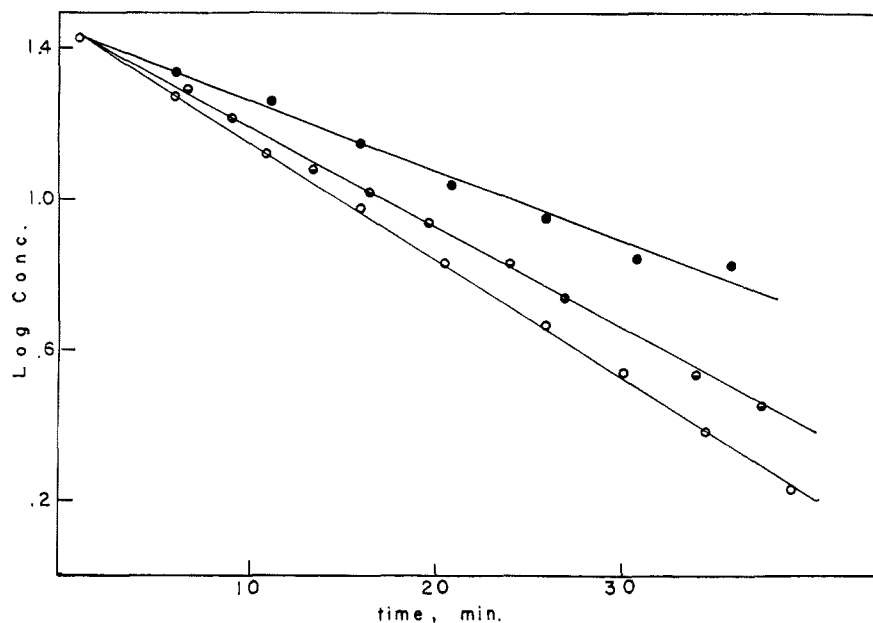(12) J. Carson and W. Miller, $J.$ $Org.$ $Chem.,$ **24**, 1814 (1959).

Figure 2.—Log concentration *vs.* time for pseudo-first-order conditions with aldehydes in ethyl acetate: ●, *p*-chloro; ◓, unsubstituted; O, *p*-methyl. Concentrations are relative rather than absolute. Table II lists pseudo-first-order rate constants.

source. Identical ozonation flasks, normally containing equivalent amounts of benzaldehyde and benzaldehyde-formyl-*d*, respectively, in the solvent, were used. Samples were removed simultaneously from each flask by two workers at 10- to 15-min. intervals during the ozonations.

An infrared method of analysis was also employed for the determination of k_H/k_D (Beer's law plots of C–D and C–H stretching vibrations), and, although the values obtained were comparable to those obtained by the n.m.r. method, the method was less reliable.

Treatment of Data.—Slopes of all lines were calculated by the method of least squares. Standard deviations were calculated for the l.f.e. plots and for the deuterium isotope effect work done by the n.m.r. method.

Gas Chromatographic Observations.—In addition to the analytical data gathered, several other pertinent details were noted.

Although many of the internal standards had been previously tested for inertness to ozone, the free radicals generated in the aldehyde ozonations might conceivably have reacted with them. Actually, the peak heights of internal standard taken before and after ozonation were identical.
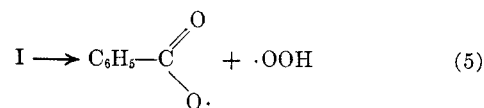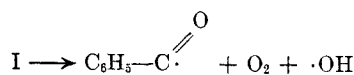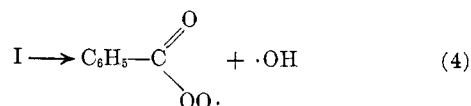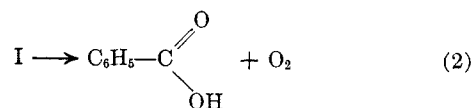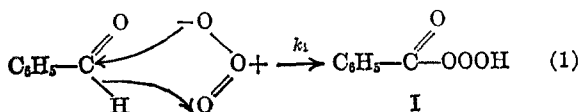
Bailey has noted that benzene is a product in benzaldehyde ozonations.[2] Gas chromatographic evidence was obtained that the corresponding benzene derivatives (*e.g.*, chlorobenzene from the chlorobenzaldehydes) were formed in ethyl acetate ozonations, although in lower yields than the 10% reported by Bailey for work in carbon tetrachloride. No benzene derivatives were noted for the work in pyridine.

For the ozonation of *p*-anisaldehyde in ethyl acetate, new peaks appeared in the chromatograms with higher retention times than the aldehydes. The fact that much more of this material appeared with the ozone–nitrogen work and that none appeared for the work in pyridine indicates that electrophilic ring attack occurs with this particular aldehyde.
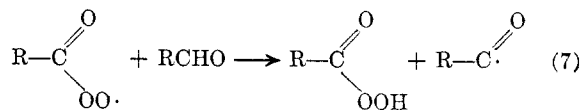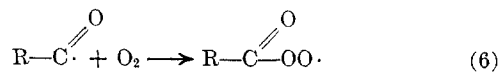
Discussion

Our kinetics (*e.g.*, Figures 1–4) are, at first thought, surprisingly good in consideration of the complicated mechanisms for ozonation of aldehydes and autoxidation which have been suggested in the literature.
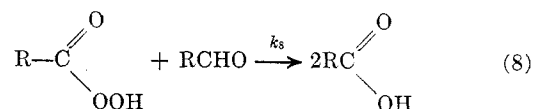
Bailey's mechanism[2] is shown by eq. 1–5.

$$\text{C}_6\text{H}_5-\text{C} \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{H}}{\Big\langle}} + \text{O} \overset{k_1}{\longrightarrow} \text{C}_6\text{H}_5-\text{C} \overset{\displaystyle \text{O}}{\diagdown}-\text{OOOH} \quad (1)$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \mathbf{I}$$

$$\mathbf{I} \longrightarrow \text{C}_6\text{H}_5-\text{C} \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{OH}}{\diagup}} + \text{O}_2 \quad (2)$$

$$\mathbf{I} \longrightarrow \text{C}_6\text{H}_5-\text{C} \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{OO}\cdot}{\diagup}} + \cdot\text{OH} \quad (4)$$

$$\mathbf{I} \longrightarrow \text{C}_6\text{H}_5-\text{C} \overset{\displaystyle \text{O}}{\cdot} + \text{O}_2 + \cdot\text{OH}$$

$$\mathbf{I} \longrightarrow \text{C}_6\text{H}_5-\text{C} \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{O}\cdot}{\diagup}} + \cdot\text{OOH} \quad (5)$$

The general mechanism for autoxidation, which was first suggested by Backstrom,[13] is shown by eq. 6 and 7.

$$\text{R}-\text{C} \overset{\displaystyle \text{O}}{\cdot} + \text{O}_2 \longrightarrow \text{R}-\text{C} \overset{\displaystyle \text{O}}{\diagup}-\text{OO}\cdot \quad (6)$$

$$\text{R}-\text{C} \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{OO}\cdot}{\diagup}} + \text{RCHO} \longrightarrow \text{R}-\text{C} \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{OOH}}{\diagup}} + \text{R}-\text{C} \overset{\displaystyle \text{O}}{\cdot} \quad (7)$$

Ordinary autoxidation, however, is complicated by the fact that perbenzoic acid undergoes reaction 8.

$$\text{R}-\text{C} \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{OOH}}{\diagup}} + \text{RCHO} \overset{k_8}{\longrightarrow} 2\text{RC} \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{OH}}{\diagup}} \quad (8)$$

Walling and McElhill eliminated this difficulty in their autoxidation study of aldehydes by carrying out their reactions in acetic anhydride solutions containing sodium acetate.[4]

White and Bailey also noted that benzene, carbon dioxide, and carbon monoxide were products of the

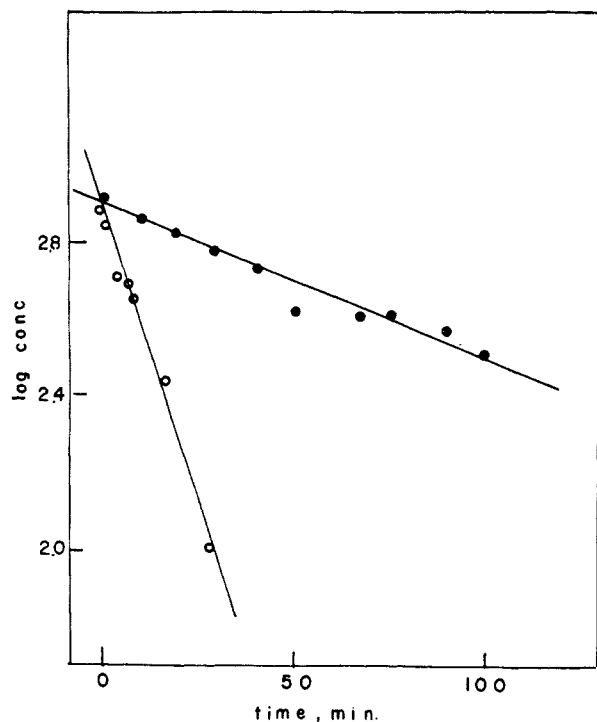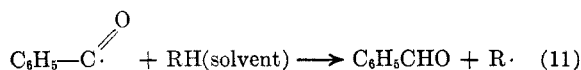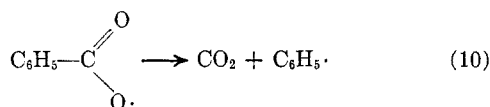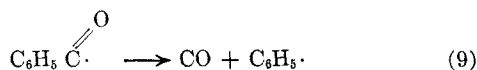(13) H. L. V. Backstrom, *Z. physik. Chem.*, **B25**, 99 (1934).

Figure 3.—Log concentration $vs.$ time for benzaldehyde-formyl-d (●) and for benzaldehyde (O) with oxygen–ozone in ethyl acetate. The ratio k_H/k_D calculated from the slopes is 7.8. Concentrations are absolute in millimoles per liter.

ozonation, suggesting steps 9 and 10.[2,14] Step 11 was also shown to occur.[2]

$$C_6H_5\overset{O}{\underset{}{\overset{\parallel}{C}}}\cdot \longrightarrow CO + C_6H_5\cdot \tag{9}$$

$$C_6H_5-\overset{O}{\underset{O\cdot}{\overset{\parallel}{C}}} \longrightarrow CO_2 + C_6H_5\cdot \tag{10}$$

$$C_6H_5-\overset{O}{\overset{\parallel}{C}}\cdot + RH(\text{solvent}) \longrightarrow C_6H_5CHO + R\cdot \tag{11}$$

Benzaldehyde can also disappear by radical paths from any of the proposed radicals $R\cdot$, $C_6H_5\overset{O}{\overset{\parallel}{C}}-O\cdot$, $\cdot OH$, $\cdot OOH$, and $C_6H_5\cdot$.

Fortunately, despite the addition of reactions 2–5 and the multitude of radicals which may react with benzaldehyde, the basic kinetic expression for the disappearance of benzaldehyde is the following.

$$\frac{-dC_6H_5CHO}{dt} =$$

$$k'[C_6H_5CHO][O_3] + k_8[C_6H_5CHO][C_6H_5\overset{O}{\overset{\parallel}{C}}-OOH] \tag{12}$$

The rate constant, k_8, must be small compared with k', since our ozonations show quite reasonable pseudo-first-order kinetics for benzaldehyde disappearance throughout the reaction even though the perbenzoic acid concentration increases. For one set of pseudo-first-order experiments, we employed sodium acetate and acetic anhydride as suggested by Walling and

(14) Since the benzoyl radical does not normally lose carbon monoxide at 0°, it seems more likely that most of the carbon monoxide reported by White and Bailey[2] came from the ozonation of solvent.
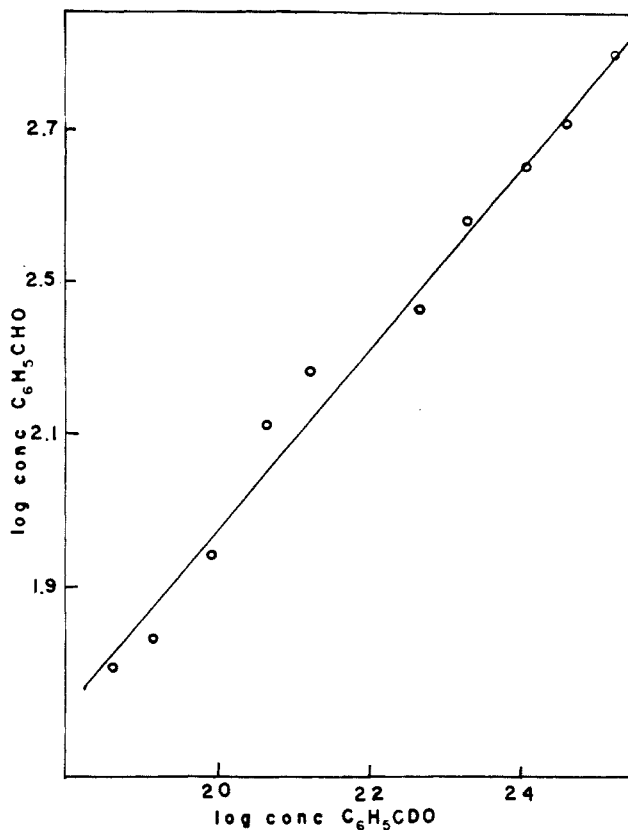

Figure 4.—Log concentration of benzaldehyde $vs.$ log concentration of benzaldehyde-formyl-d. Data were obtained from simultaneous ozonations in two flasks in carbon tetrachloride with ozone–nitrogen. The slope, k_H/k_D, 1.18, was obtained by least-square statistics on all experimental points. Concentrations are absolute in millimoles per liter.

McElhill[4] and found no appreciable change in the over-all rate constant.

The rate constant, k', of eq. 12 and the relative rate constants which we have determined in ethyl acetate are composed of many rate constants, while our major interest is in the determination of the rate constants, k_1, for various substituted aldehydes. The basic stoichiometry for ozone–oxygen ozonations is such that only about 0.4 mole of ozone is required for each mole of aldehyde consumed. On the other hand, White and Bailey[2] have shown (and we have confirmed their results) that more than 1 mole equiv. of ozone is required for each mole of aldehyde in ozone–nitrogen work. Thus, reactions 6 and 7 are considerably more important in the ozone–oxygen work and reaction 11 is of some importance in the ozone–nitrogen work.

Ozonation of benzaldehyde in pyridine with an oxygen–ozone stream is approximately one-seventh as fast as in ethyl acetate. Part of this decreased rate could be due to a competitive reaction with pyridine or pyridine N-oxide, but under our conditions ozone was not quantitatively absorbed and a good log concentration $vs.$ time plot was obtained for the disappearance of benzaldehyde. The ozonized pyridine–benzaldehyde solution showed only a weak potassium iodide test for active oxygen. Because of these observations, we feel that autoxidation is effectively stopped by carrying out the ozonations in pyridine[15]

(15) Pyridine is probably reducing the initial product of aldehyde and ozone to yield pyridine N-oxide.

and that the relative rates determined in this solvent are a measure of the selectivity of ozone, i.e., a truer measure of k_1 from reaction 1.

Table I lists the relative rates for appropriately substituted aldehydes under the three sets of conditions employed. Figures 5–7 are linear free-energy plots of these results and yield the ρ values of -1.10 ± 0.09, -0.94 ± 0.12, and -0.58 ± 0.10 for ozone–oxygen, ozone–nitrogen, and ozone–oxygen in pyridine, respectively.

TABLE I

RELATIVE RATES vs. BENZALDEHYDE. COMPETITIVE METHOD

Substituent	O_3–O_2, ethyl acetate	O_3–N_2, ethyl acetate	O_3–O_2, pyridine
p-MeO	2.16	2.30	1.46
p-Me	1.62	1.36	1.13[a]
m-Me	1.20	1.13	1.2
None	1	1	1
p-Cl	0.62	0.58	0.715[b]
p-Br	0.56	0.67	0.68
m-Cl	0.42	0.44	0.60
m-Br	0.39	0.39	0.63
o-Me		2.7	
o-NO₂		0.12	
2,4,6-Me₃			7.2

[a] Value determined with ozone–nitrogen was 1.14. [b] Value determined with ozone–nitrogen was 0.72.

Table II summarizes the relative rates obtained by the pseudo-first-order method. Generally, the results are the same as by the competitive method. However, in the competitive method two different radicals (e.g., $C_6H_5C(=O)OO\cdot$ and p-$ClC_6H_4C(=O)OO\cdot$ from their respective aldehydes) were always present. Since (as shown by Walling and McElhill[4]) these radicals would have slightly different selectivities, it is reasonable that the relative rates determined by the pseudo-first-order method should be slightly lower.

TABLE II

PSEUDO-FIRST-ORDER RELATIVE RATES

Compd.	k^a	Relative rate	Av.
p-Tolualdehyde	0.0331, 0.0341, 0.0353	1.25, 1.35, 1.28	1.29
Benzaldehyde[b]	0.0264, 0.0252, 0.0278	1	1
p-Chlorobenzaldehyde	0.0189, 0.0192, 0.0194	0.72, 0.76, 0.74	0.74

[a] k is a rate constant determined from the slope of the line of a log concentration vs. time plot and does not include the concentration of ozone, which is constant for each run. [b] Under the same conditions in pyridine, k is 0.0032.

Table III, summarizes the work on the deuterium isotope effect for various ozonation conditions.

TABLE III

DEUTERIUM ISOTOPE EFFECT FOR ALDEHYDE OZONATIONS

Reaction	Solvent	Method	$k_H/k_D{}^a$
O_3–O_2	Ethyl acetate	N.m.r.	7.8 ± 0.7
O_3–O_2	Carbon tetrachloride	Infrared	6[b]
O_3–N_2	Ethyl acetate	N.m.r.	1.4 ± 0.08
O_3–N_2	Carbon tetrachloride	N.m.r.	1.2 ± 0.05
O_3–N_2	Carbon tetrachloride	Infrared	1.9, 2.0[b]
O_3–O_2	Pyridine	N.m.r.	3.3 ± 0.6
O_3–N_2	Pyridine	N.m.r.	2 ± 0.3

[a] All k_H/k_D values were determined at 0°. [b] The results from the infrared method are for only four or five points per run and no standard deviation was calculated. They are probably accurate only to ±20%. The competitive method was used for these determinations.
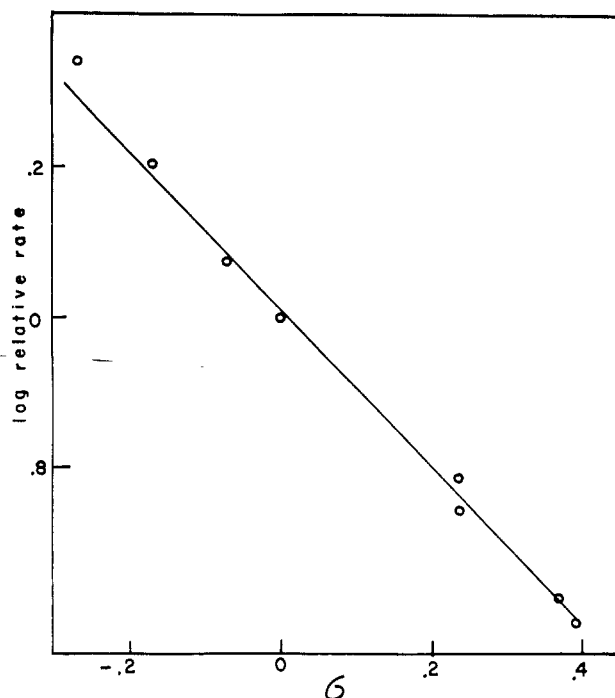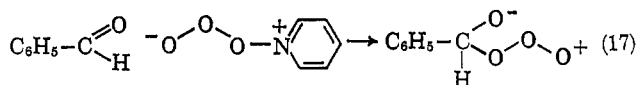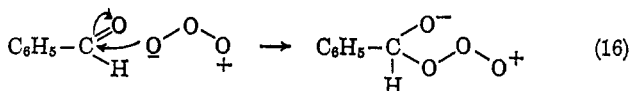

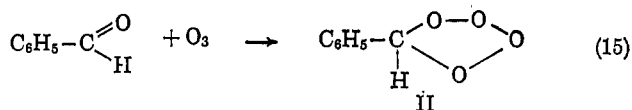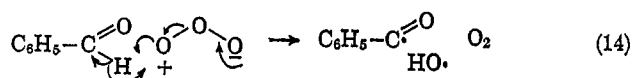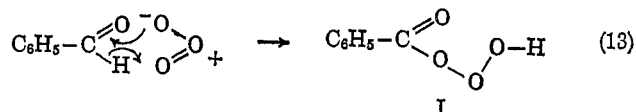Figure 5.—Hammett σ values for substituents of substituted benzaldehydes vs. log relative rate constants for ozone–oxygen work in ethyl acetate. The ρ value is -1.10 ± 0.09.

The following initial steps for the mechanism of the ozonation of aldehydes may be considered.

$$C_6H_5-C\overset{O}{\underset{H}{\diagdown}}\overset{-O}{\diagup}\overset{O}{\diagdown}O + \quad \rightarrow \quad C_6H_5-C\overset{O}{\diagup}\overset{O}{\diagdown}{\overset{O}{\diagup}}O-H \quad (13)$$
$$\text{I}$$

$$C_6H_5-C\overset{O}{\underset{H}{\diagdown}}\overset{O}{\diagup}\overset{O}{\diagdown}O + \quad \rightarrow \quad C_6H_5-C\overset{O}{\diagdown} \quad O_2 \quad (14)$$
$$HO\cdot$$

$$C_6H_5-C\overset{O}{\underset{H}{\diagdown}} + O_3 \quad \rightarrow \quad C_6H_5-C\overset{O-O}{\underset{H}{\diagdown}}O \quad (15)$$
$$\text{II}$$

$$C_6H_5-C\overset{O}{\underset{H}{\diagdown}}O\overset{O}{\diagup}\overset{O}{\diagdown}O + \quad \rightarrow \quad C_6H_5-C\overset{O^-}{\underset{H}{\diagdown}}O\overset{O}{\diagup}\overset{O^+}{\diagdown} \quad (16)$$

$$C_6H_5-C\overset{O}{\underset{H}{\diagdown}} \quad {}^-O\overset{O}{\diagup}\overset{O}{\diagdown}O-\overset{+}{N}\diagup\!\!\diagdown \rightarrow C_6H_5-C\overset{O^-}{\underset{H}{\diagdown}}O\overset{O}{\diagup}\overset{O^+}{\diagdown} \quad (17)$$

Reactions 16 and 17 involve nucleophilic attack of ozone, and our ρ values show that these mechanisms are inoperative even in pyridine. Reaction 14, in which ozone is acting as a radical initiator, as appealing in terms of the increase in bond energies of the products (and therefore of the transition state) but is excluded on the grounds of the low deuterium isotope effect found with ozone–nitrogen streams in ethyl acetate and carbon tetrachloride.

Our data do not distinguish between reactions 13 and 15. Reaction 13, which was proposed by White and Bailey, is essentially an insertion reaction into a σ bond and is similar to an intermediate proposed by Price[16] for the ozonation of ethers. Our ρ value is

(16) C. C. Price and A. L. Tumolo, J. Am. Chem. Soc., 86, 4691 (1964).
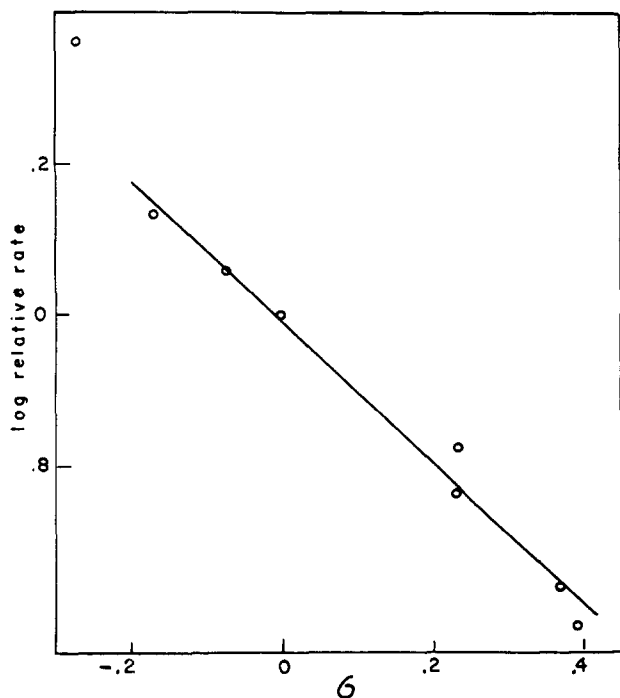
Figure 6.—Hammett σ values for substituents of substituted benzaldehydes vs. log relative rate constants for ozone–nitrogen work in ethyl acetate. The ρ value is -0.94 ± 0.12. The point for anisaldehyde ($\sigma = -0.27$) was not included in the least-square treatment because of gas chromatographic evidence for competing ring attack.

Figure 7.—Hammett σ values for substituents of substituted benzaldehydes vs. log relative rate constants for ozone–oxygen work in pyridine. The ρ value is -0.58 ± 0.10.

consistent with such a mechanism and the low k_H/k_D values (1.2 to 1.4) are possible for nonlinear transition states.

Reaction 15 has an analogy in the five-membered ring formed in the ozonation of alkenes, and work in our laboratory[17] suggests that substituted benzaldehyde Schiff bases (relative reactivity sequence, p-Me > p-H > p-NO$_2$) react with ozone to yield a similar five-membered ring. If reaction 15 were rate determining, the deuterium isotope effect would be around 1 for ozone attack and increased in proportion to the amount of radical attack. Thus, reaction 15 is also consistent with our data for ozonations in ethyl acetate and carbon tetrachloride.[18] Intermediate II might then rearrange to I which could undergo homolytic cleavage to radicals, as suggested by White and Bailey. It has been noted by Huisgen that reactions such as (15) are unlikely energetically.[19]

The data from pyridine are harder to reconcile with any of the reactions mentioned. It could be argued

that the lower ρ value indicates some nucleophilic attack, but the increased (relative to ozone–nitrogen in carbon tetrachloride) deuterium isotope effect suggests that this is not the case. Aldehydes are probably strongly solvated in pyridine, and ozone may actually be attacking a pyridine–aldehyde complex. The value for a reaction between an ozone–pyridine complex (which should have increased electrophilic selectivity) and a pyridine–aldehyde complex (which should be less selectively attacked) would have been difficult to predict beforehand.

The isotope effect data determined in pyridine, $k_H/k_D = 3.3 \pm 0.5$ for ozone–oxygen and $k_H/k_D = 2.0 \pm 0.3$ for ozone–nitrogen, indicate that a small amount of autoxidation may be occurring even in this solvent. The value of 2.0 $\pm$ 0.3 may indicate a slightly different transition state, one involving more carbon–hydrogen bond breakage, than in carbon tetrachloride or ethyl acetate.

Finally, it may be noted from the data in Table I on o-tolualdehyde, o-nitrobenzaldehyde, and mesitaldehyde, that there is no serious steric hindrance to the reaction of ozone with aldehydes. This fact may also point to reaction 13 rather than (15) as the initial step in the attack of ozone on aldehydes.

(17) P. Andrulis, M.S. Thesis, Canisius College, 1964.

(18) The possibility of reaction 11 occurring in the ozone–nitrogen work in ethyl acetate was our major reason for doing work in carbon tetrachloride. Our method of analysis would have resulted in low experimental values of k_H/k_D if the true value of k_H/k_D had been high and if reaction 11 had been significant. Benzoyl chloride, the corresponding product from reaction 11 in carbon tetrachloride, did not interfere with our analysis.

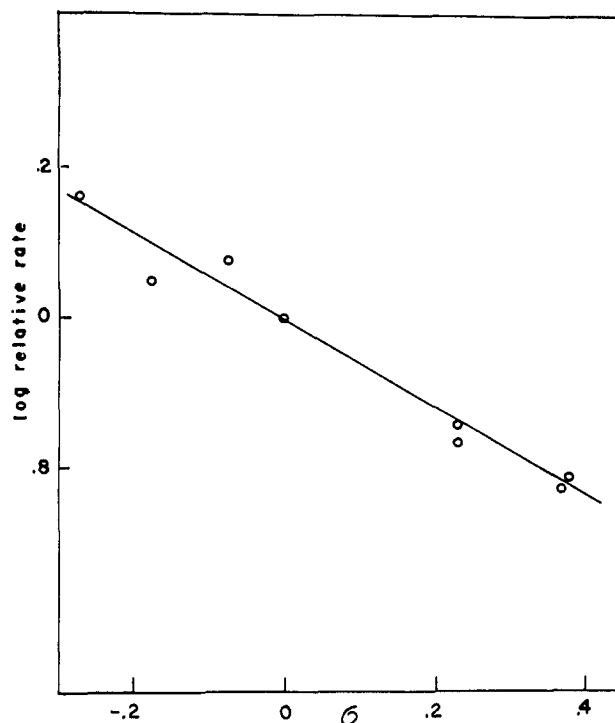(19) R. Huisgen, Angew. Chem. Intern. Ed. Engl., 2, 641 (1963).