wise available[20]: 2-phenyl, 2-phenyl-8-methyl, 2-phenyl-6,8-dimethyl, 2-*o*-tolyl, and 2-*p*-tolyl.

2-*p*-Hydroxyphenyl-4(1H)-quinolone.—2-*p*-Anisyl-3-acetyl-4(1H)-quinolone and concentrated hydrochloric acid formed IV (R_1 = H; Ar = *p*-HOC_6H_4) in almost theoretical yield. It was crystallized from dilute ethanol and was obtained as a monohydrate, m.p. 175–180°.

Anal. Calcd. for $C_{15}H_{11}NO_2 \cdot H_2O$: N, 5.49. Found: N, 5.52.

Dehydration was effected by heating at ~200°, and the resolidified base (m.p. ~280°) was recrystallized from glacial acetic acid and gave IV (R_1 = H; Ar = *p*-HOC_6H_4) as colorless platelets, m.p. 284–285° (lit.[21] m.p. 216°).

Anal. Calcd. for $C_{15}H_{11}NO_2$: N, 5.91. Found: N, 5.71.

The absence of methoxyl in the anhydrous sample was confirmed by a Zeisel determination and also by the infrared spectrum which, in contrast to the spectra of III (R_1 = H; Ar = *p*-$CH_3OC_6H_4$) and IV (R_1 = H; Ar = *p*-$CH_3OC_6H_4$), showed no strong methoxyl band in the 9.7–9.8-μ region.

2-*p*-Hydroxyphenyl-4(1H)-quinolone, m.p. 284–285°, was likewise produced on subjecting 2-*p*-anisyl-4(1H)-quinolone and 2-*p*-anisyl-3-carboxy-4(1H)-quinolone, respectively, to a similar degradation. Confirmation of its structure was obtained by cyclization of methyl β-amino-α-(N-phenyl-*p*-hydroxybenzimidoyl)crotonate (I, Ar = *p*-HOC_6H_4; Ar′ = C_6H_5, 0.15 g.) in liquid paraffin (2 g.) at 250° for 5 min.; the product (0.1 g., 87%) separated from dilute ethanol as a hydrate, m.p. 175–180°, and was converted to the anhydrous base, m.p. 284–285°, which proved to be identical (mixture melting point and infrared spectrum) with the product from degradation of 2-*p*-anisyl-3-acetyl-4(1H)-quinolone.

2-Phenyl-3-acetyl-4-anilinoquinoline (VIII, R_1 = H).—A two-molar proportion of aniline (0.33 g.) was stirred with 2-phenyl-3-acetyl-4-chloroquinoline (0.5 g.) on the water bath for 15 min. The solidified mixture was dissolved in ethanol and the 4-anilinoquinoline was precipitated in good yield (0.6 g.) by the addition of water. A recrystallization from dilute ethanol furnished ether-soluble, pale yellow needles, m.p. 114–116°, insoluble in dilute alkali and readily soluble in dilute hydrochloric acid to give a bright yellow solution.

Anal. Calcd. for $C_{23}H_{18}N_2O$: N, 8.28; mol. wt., 338. Found: N, 8.26; mol. wt., 310.

The infrared spectrum showed NH and CO absorption at 3.1 and 6.03 μ, respectively, and was in keeping with the structure assigned.

2-*p*-Anisyl-3-acetyl-4-anilinoquinoline was similarly obtained from VII (R_1 = H; Ar = *p*-$CH_3OC_6H_4$) in 60% crude yield, yellow needles from dilute ethanol, m.p. 121–123° (lit.[6] m.p. 213–214°); NH and CO bands were at 3.05 and 6.02 μ, respectively.

Anal. Calcd. for $C_{24}N_{20}N_2O_2$: N, 7.61. Found: N, 7.82.

6-Phenyl-7-methyldibenzo[*b,h*][1,6]naphthyridine (X).—VIII, 2-Phenyl-3-acetyl-4-anilinoquinoline (0.25 g.), was stirred with PPA (3 g.) at 150° for 30 min., the reaction proceeding with effervescence. The solution was cooled and neutralized with dilute sodium hydroxide and the precipitated product was collected and recrystallized from acetic acid, pale brown needles, m.p. 178–180°. These were sparingly soluble in dilute hydrochloric acid, ether, and ethanol.

Anal. Calcd. for $C_{23}H_{16}N_2$: N, 8.75; mol. wt., 320. Found: N, 8.59; mol. wt., 297.

The infrared spectrum showed no NH or carbonyl absorption and was consistent with structure X.

2,4-Diphenyl-3-methyl-2H-pyrazolo[4,3-*c*]quinoline (XI).—Equimolar proportions of 2-phenyl-3-acetyl-4-chloroquinoline (1.1 g.) and phenylhydrazine (0.45 g.) were stirred together at 140° for 30 min. The mixture liquified and effervesced and became semisolid. It was cooled and triturated with ether to yield a fawn-colored powder (1.3 g.), m.p. 250–260°, which was possibly a hydrochloride. This was recrystallized from dilute ethanol and formed colorless platelets, m.p. 185–186°, insoluble in dilute sodium hydroxide.

Anal. Calcd. for $C_{23}H_{17}N_3$: N, 12.54; mol. wt., 335. Found: N, 12.75; mol. wt., 317.

The infrared spectrum of XI, like that of the isomeric 1,4-diphenyl isomer,[3] showed no NH and no carbonyl absorption; significant differences between the two spectra were, however, evident in the 6–7- and 10–11-μ regions particularly.

---

[20] B. Staskun and S. S. Israelstam, *J. Org. Chem.*, **26**, 3191 (1961).

[21] K. Dziewoński and J. Mayer, *Roczniki Chem.*, **14**, 1157 (1935); *Chem. Abstr.*, **29**, 6599 (1935).

Ozonation of Aromatic Aldehydes[1]

HAROLD M. WHITE AND PHILIP S. BAILEY[2]

Department of Chemistry, The University of Texas, Austin, Texas 78712

Received March 9, 1965

The order of reactivity with ozone–nitrogen mixtures for the aromatic aldehydes studied was anisaldehyde > benzaldehyde > *p*-nitrobenzaldehyde, showing that a nucleophilic ozone attack on the carbonyl group of the aldehyde is not an important, or rate-determining, step. The major product from ozone attack on benzaldehyde is perbenzoic acid whether ozone–nitrogen or ozone–oxygen mixtures are employed. Much more ozone is required per benzaldehyde molecule with ozone–nitrogen than with ozone–oxygen, however. It is suggested that the predominant ozone attack on an aromatic aldehyde is a concerted 1,3-dipolar insertion, producing unstable intermediate ArC(=O)OOOH, which decomposes, predominantly, to aroylperoxy radicals. These produce peracids by abstraction of hydrogen from the solvent or the aldehyde. Therefore, autoxidation, which occurs in the presence of oxygen, is initiated by these radicals rather than by ozone itself.

The ozonation of aldehydes has been studied by several investigators, including Harries,[3] Fischer,[4] Briner,[5] Spath,[6] von Wacek,[7] and Dick.[8] Harries[3] studied aliphatic aldehydes and reported that a peroxidic intermediate was produced which rearranged to the corresponding acid. He represented the reaction as follows: $RCHO + O_3 \rightarrow O_2 + RC(H){=}O{=}O \rightarrow RC({=}O)OH$. Other workers found that not only the carboxylic acid but also the peracid,[4,5,8] and with some aromatic aldehydes the corresponding phenol,[6,7] is produced. Fischer, Düll, and Volz[4] suggested an initial adduct between ozone and the aldehyde ($RCH{=}O \cdot O_3$) which then can react with another mole of aldehyde to give 1 mole of acid and 1 mole of peracid, or with 2 moles of aldehyde to give 3 moles of acid. Briner and co-workers[5] studied the oxidation of benzaldehyde with ozone–oxygen–nitrogen mixtures of various ozone–oxygen ratios. When present in high concentration,

---

[1] Presented in part at the Ozone Symposium held at the 19th Southwest Regional Meeting of the American Chemical Society, Houston, Texas, Dec. 1963.

[2] To whom inquiries should be directed.

[3] (a) C. Harries and K. Langheld, *Ann.*, **343**, 345 (1905); (b) C. Harries, *ibid.*, **374**, 288 (1910); (c) C. Harries and R. Koetschau, *ibid.*, **374**, 321 (1910).

[4] F. G. Fischer, H. Düll, and J. L. Volz, *ibid.*, **486**, 80 (1931).

[5] E. Briner, Advances in Chemistry Series, No. 21, American Chemical Society, Washington, D. C., 1959, p. 184, and earlier references therein.

[6] E. Späth, M. Pailer, and G. Gergely, *Ber.*, **73**, 795 (1940).

[7] A. v. Wacek and H. O. Eppinger, *ibid.*, **73**, 644 (1940).

[8] C. R. Dick and R. F. Hanna, *J. Org. Chem.*, **29**, 1218 (1964).

TABLE I

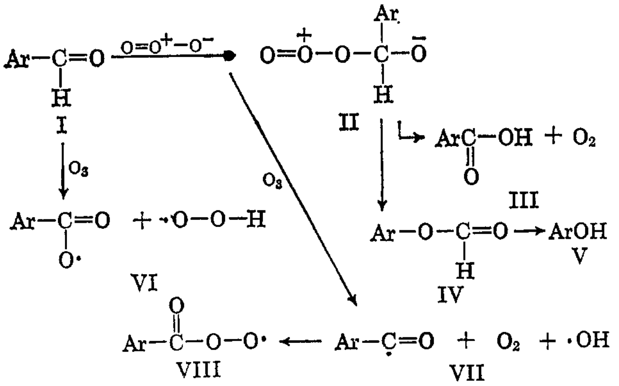
OZONATION OF BENZALDEHYDE WITH OZONE–NITROGEN MIXTURES AT 0 TO 5°[a]

Expt.	Solvent	O_3 employed,[b] mole equiv.	Work-up[c] procedure	O_2 evolved,[d] mole equiv.	Perbenzoic acid,[d] mole equiv.	Benzoic acid,[d,e] mole equiv.	Recovered benzaldehyde,[d] mole equiv.	Benzene,[d] mole equiv.
1	CH_2Cl_2	1	A	0.22–0.30	0.23–0.30	0.15–0.17	0.30–0.35	0.1
2	CH_2Cl_2	1	B	0.22–0.30		0.55–0.64[f]	0.15	0.1
3	$CHCl_3$	1	A		0.27	0.13	0.18	
4	CCl_4	1	A	0.22	0.23	0.36[g]	0.2–0.25[h]	
5	CCl_4	1	B	0.22–0.30		0.58[f]		
6	Glacial[i] acetic acid	1	A	0.16	0.23	0.21		
7	CH_2Cl_2	0.5	A		0.15[j]	0.01[j]	0.72[j]	
8	CH_2Cl_2	0.5	B		0.15	0.30[k]	0.55	
9	CH_2Cl_2	2.0	A	0.75		0.55[f]	0.17	
10	CH_2Cl_2	3.0[l]	A	1.1		0.45[f]	0.0	
11[m]	CH_2Cl_2	1.0	A		0.1	0.16	0.56[m]	

[a] No entry in a column means that the quantity was not determined. Where a range is given, this is the result of several experiments. [b] In all experiments except 4, 5, and 10, the ozone was essentially quantitatively absorbed. With CCl_4 solvent (experiments 4 and 5) the absorption throughout was 80–90%. [c] See Experimental section. [d] Yields are given in moles per mole of benzaldehyde started with. [e] In all except experiments 2, 5, 8, 9, and 10, the benzoic acid yield recorded is the total yield after reductive or heat decomposition minus the perbenzoic acid yield found before reduction or decomposition to benzoic acid. [f] This is total benzoic acid yield after work-up and includes, therefore, the perbenzoic acid yield. [g] This includes approximately 0.2 mole equiv. of benzoyl chloride shown by infrared spectrum to be present before work-up and which was hydrolyzed during work-up. [h] Less than 0.02 mole equiv. of unreacted benzaldehyde was present after 2 mole equiv. of ozone (only about 75% of which actually reacted) had been passed through the reaction mixture. [i] In this experiment the reaction temperature was 25°. [j] In this experiment, the reduction was carried out immediately before any interaction between perbenzoic acid and benzaldehyde to give benzoic acid could occur. [k] This is the total benzoic acid yield after heat decomposition, and obviously shows that the perbenzoic acid found before decomposition (0.15 mole equiv.) oxidized 1 equiv. of benzaldehyde during the decomposition (*cf.* experiment 7). [l] Ozone absorption was not quantitative after 2 mole equiv. and a total of only 2.6 mole equiv. reacted. [m] In this experiment the reaction temperature was −30°.

oxygen appeared to be the principal reactant, provided that traces of ozone were also present. Briner[5] considered this to be evidence for an ozone-initiated autoxidation. Briner[5] also reported that the perbenzoic–benzoic acid ratio decreased with decreasing oxygen content in the stream, until essentially only benzoic acid resulted when the gas mixture was 1:1:98%, respectively. Dick[8] has reported near quantitative yields of perbenzoic acid from benzaldehyde using ozone–oxygen mixtures.

In a review[9] of the literature up to 1958, it was suggested that in the absence of oxygen ozone attacks the carbonyl group of an aldehyde nucleophilically (*e.g.*, I → II), as proposed earlier by Leffler,[10] whereas in the presence of oxygen ozone serves as a radical initiator (*e.g.*, I → VI, as proposed by Schubert and Pease[11] for alkane autoxidations, or I → VII). Both oxidation to the acid (II → III) and formation of phenols (II → IV → V) can be explained by the nucleophilic mechanism.



The principal flaw in the preceding proposal is that the mere presence or absence of oxygen should cause the actual ozone attack to be completely different, radical in one case and ionic in the other. For this reason it was decided to study the ozonation of aromatic aldehydes further. Since most of the earlier investigations (except a few of Briner's[5] experiments) were with ozone–oxygen mixtures, the reaction of ozone itself with aldehydes has been obscured. Thus, most of our work has been with ozone–nitrogen mixtures[12–15] and with benzaldehyde. Comparisons also were made with anisaldehyde and *p*-nitrobenzaldehyde in order to obtain evidence for or against the nucleophilic ozone attack mechanism.

The reaction of a methylene chloride solution of benzaldehyde with ozone from an ozone–nitrogen mixture was found to proceed with essentially quantitative absorption of ozone at temperatures ranging from −20 to 25°. In most experiments the reaction was stopped after the absorption of 1 mole equiv. of ozone, and the reaction mixture was either reduced with sodium iodide or decomposed by heat. Typical experiments yielded, after the reductive work-up, 0.40–0.45 mole equiv. of benzoic acid, 0.30–0.35 mole equiv. of recovered benzaldehyde, and about 0.1 mole equiv. of benzene (Table I, experiment 1). From the heat decomposition work-up experiments, there was obtained 0.55–0.64 mole equiv. of benzoic acid, about 0.15 mole equiv. of unreacted

---

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

(10) J. E. Leffler, *ibid.*, **45**, 385 (1949).

(11) C. C. Schubert and R. N. Pease, *J. Am. Chem. Soc.*, **78**, 2044, 5553 (1956).

(12) G. A. Cook, A. D. Kiffer, C. V. Klumpp, A. H. Malik, and L. A. Spence, Advances in Chemistry Series, No. 21, American Chemical Society, Washington, D. C., 1959, p. 44.

(13) P. S. Bailey and A. M. Reader, *Chem. Ind.* (London), 1063 (1961).

(14) P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *J. Org. Chem.*, **29**, 1400 (1964).

(15) A. M. Reader, P. S. Bailey, and H. M. White, *ibid.*, **30**, 784 (1965).

benzaldehyde, 0.1 mole equiv. of benzene, and a trace of phenol (Table I, experiment 2).

Under similar conditions anisaldehyde quantitatively absorbed 1 mole equiv. of ozone and, after the reductive work-up, 0.54 mole equiv. of anisic acid and 0.28 mole equiv. of recovered anisaldehyde were obtained. The absorption of ozone by *p*-nitrobenzaldehyde under the same conditions, however, was slow. Only 0.65 mole equiv. of ozone was absorbed by 1 mole equiv. of *p*-nitrobenzaldehyde from an ozone–nitrogen stream containing 1 mole equiv. of ozone. After a thermal decomposition, 0.08 mole equiv. of *p*-nitrobenzoic acid and 0.74 mole equiv. of recovered *p*-nitrobenzaldehyde were obtained.

It is obvious from these results that *p*-nitrobenzaldehyde is considerably less reactive toward ozone than is benzaldehyde, and, judging from a comparison of the benzoic and anisic acid yields, anisaldehyde is somewhat more reactive than benzaldehyde. If the ozone attack on the aldehyde had been nucleophilic, as shown in I → II → III, the results should have been just the opposite. Thus, the nucleophilic ozone attack mechanism appears to be invalid, even with ozone–nitrogen mixtures.

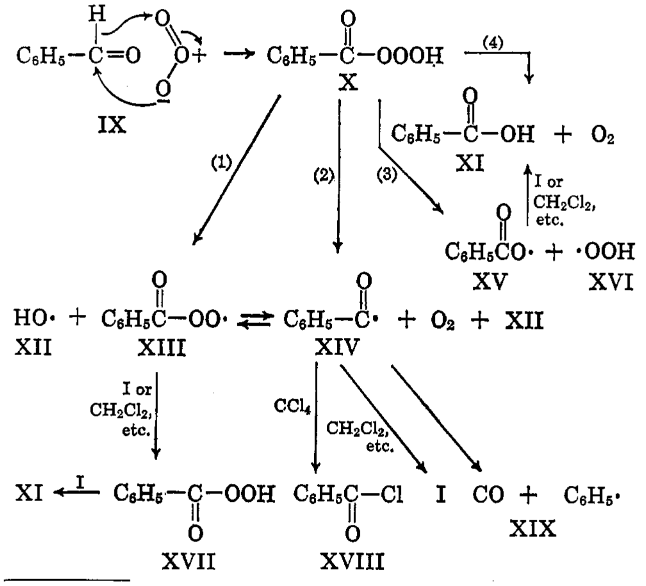
Molecular oxygen (0.22–0.30 mole equiv.) was evolved during ozonations of benzaldehyde with 1 mole equiv. of ozone from ozone–nitrogen. Infrared analysis of the reaction mixture showed the presence of 0.23–0.30 mole equiv. of perbenzoic acid in addition to benzoic acid and unreacted benzaldehyde. Iodimetric determination of the active oxygen content showed it to be equal to the perbenzoic acid yield. Therefore, the benzoic acid yield after reduction is equal to the combined perbenzoic acid and benzoic acid yields before reduction, as shown in Table I, experiment 1. Data on reactions worked up by heating are summarized in Table I, experiment 2. Carbon monoxide and carbon dioxide were detected in the off gases during various ozonations.

Results of ozonation of benzaldehyde in methylene chloride solution with 0.5, 2, and 3 mole equiv. of ozone from ozone–nitrogen mixtures are shown in Table I. A comparison of the results obtained from a reductive *vs.* a heat decomposition work-up in the case of the 0.5 and the 1 mole equiv. of ozone reactions shows that the yields of benzoic acid from the heat decomposition reactions were considerably higher than the benzoic acid yields (*i.e.*, combined yield of benzoic acid already present and that produced by reduction of perbenzoic acid), from the reduction experiments. In the case of the 0.5 mole equiv. of ozone experiments, especially, (*cf.* Table I, experiments 7 and 8) the data show clearly that during the heat decomposition 1 mole of perbenzoic acid oxidizes 1 mole of benzaldehyde to benzoic acid.

Ozonations of benzaldehyde with 1 mole equiv. of ozone also were run in glacial acetic acid, chloroform, and carbon tetrachloride solutions. The results were similar to those obtained in methylene chloride (Table I; *cf.* experiments 1–6), except for the carbon tetrachloride experiment (Table I, experiment 4). In this case the benzoic acid yield, after the reductive work-up, was considerably higher than that obtained under similar conditions from the other reaction mixtures (by about 0.2 mole equiv.; *cf.* Table I, experiments 1 and 4). Infrared analysis of the reaction mixture before reduction showed the presence of benzoyl chloride in an amount approximately equal to the extra benzoic acid found after reduction.[16]

The formation of carbon monoxide, carbon dioxide, benzene, and benzoyl chloride during ozonation of benzaldehyde with ozone–nitrogen mixtures suggests that even in these reactions radicals are produced. In fact, it could be argued from the results described that ozone attacked benzaldehyde (I) in a radical fashion to give molecular oxygen and benzoyl and hydroxy radicals (products VII). Interaction of the benzoyl radicals and molecular oxygen would give benzoylperoxy radicals (VIII), and abstraction of hydrogen from the environment by these radicals would explain the perbenzoic acid obtained.

We do not favor this mechanism, however, since the microwave spectrum of ozone does not indicate any radical character,[17] and all of the other reactions of ozone appear to be of an ionic nature.[9] Instead, we suggest that ozone attacks benzaldehyde by means of a 1,3-dipolar insertion reaction to give an unstable intermediate (X)[18] which then breaks down to give radicals. This insertion reaction is pedagogically similar to the 1,3-dipolar cycloadditions of Huisgen[19] which include the addition of ozone to a carbon–carbon double bond to give an initial ozonide.[19] It could be described as a concerted hydride ion abstraction from the aldehyde carbonyl group by the positive end of the ozone molecule and a simultaneous attack by the negative end of the ozone molecule on the developing acylium ion, as shown by IX → X. Such a mechanism would explain the order of reactivity observed with anisaldehyde, benzaldehyde, and *p*-nitrobenzaldehyde, just as the 1,3-dipolar cycloaddition mechanism explains the retardation of ozone attack on a double bond by electron-withdrawing groups.



---

(16) C. S. Marvel and V. Nichols [*J. Org. Chem.*, **6**, 296 (1941)] reported a 15% yield of benzoyl peroxide from ozonation of benzaldehyde in carbon tetrachloride. This probably arose by interaction of benzoyl chloride and perbenzoic acid during the work-up, which involved alkaline conditions.

(17) (a) R. Trambarulo, S. N. Ghosh, C. A. Burrus, Jr., and W. Gordy, *J. Chem. Phys.*, **21**, 851 (1953); (b) R. H. Hughes, *ibid.*, **24**, 131 (1956).

(18) Such an intermediate was suggested at the Ozone Symposium of the 19th Southwest Regional Meeting of the American Chemical Society, Houston, Texas, Dec. 1963, independently, both by us (paper by H. M. White, J. E. Batterbee, and P. S. Bailey), to explain the above results, and by Price to explain results from the ozonation of ethers: see C. C. Price and A. L. Tumolo, *J. Am. Chem. Soc.*, **86**, 4691 (1964).

(19) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565, 633 (1963).

The unstable intermediate X could then decompose by at least four different routes: (1) to benzoylperoxy radicals (XIII), (2) to benzoyl radicals (XIV), (3) to benzoyloxy radicals (XV), and (4) to benzoic acid and molecular oxygen, directly. The first of these is considered to be the predominant decomposition route since the experiments with 0.5 mole equiv. of ozone (Table I, experiment 7) show that mostly perbenzoic acid and very little benzoic acid are present early in the reaction. Perbenzoic acid (XVII) could be produced by abstraction of hydrogen from either unreacted benzaldehyde or the solvent by the benzoylperoxy (XIII) radicals. Most of the benzoic acid appears to be produced *via* the slow oxidation of unreacted benzaldehyde by perbenzoic acid (a reaction which occurs vigorously during the heat decomposition work-up) rather than by route 4 or route 3 and abstraction of hydrogen by the benzoyloxy radical (XV). Further evidence for this comes from the fact that infrared spectra of the reaction mixture taken at intervals showed that the amounts of perbenzoic acid and benzaldehyde in the reaction mixture slowly decreased while that of benzoic acid increased correspondingly. The phenols found by Späth[6] and von Wacek[7] from ozonation of methoxylated benzaldehydes were probably produced by a Baeyer–Villiger[20] reaction between the aldehyde and the peracid. Only traces of phenol were found in the present research, as would be expected because of the lower migratory aptitude of the phenyl group. Under more polar decomposition conditions, however, the phenol yield increased to 1–2%.

The occurrence of benzoyl chloride (XVIII) in the products from ozonation of benzaldehyde in carbon tetrachloride is evidence for the presence of benzoyl radicals (XIV), which could be produced in several ways: (1) from X *via* route 2, (2) by loss of molecular oxygen from the benzoylperoxy radical (XIII) or, most likely, (3) by abstraction of hydrogen from unreacted benzaldehyde by radicals such as XII, XIII, XV, XVI, or XIX. In methylene chloride, chloroform, or glacial acetic acid, the benzoyl radical apparently regenerates benzaldehyde by abstraction of hydrogen from the solvent. This accounts for the higher yield of benzoic acid from the 1 mole equiv. of ozone reaction in carbon tetrachloride (hydrolysis of benzoyl chloride during work-up) than from the other solvents (*cf.* Table I, experiments 1, 3, 4, and 6). The fact that between 2 and 3 mole equiv. of ozone is required to use up completely benzaldehyde (Table I, experiments 9 and 10) is also indicative of the continuous regeneration of benzaldehyde in methylene chloride solution. In carbon tetrachloride solution, much less unreacted benzaldehyde is present after reaction with 1 or 2 mole equiv. of ozone than in methylene chloride solution (*cf.* Table I, experiments 1, 4, 9, and 10). The presence of benzene and carbon monoxide among the products further indicates the production of benzoyl radicals during the ozonation (XIV → XIX). Benzene also could be produced *via* decomposition of radical XV to XIX and carbon dioxide.

There are several facets of our data which, admittedly, are somewhat difficult to explain. One is that, whereas in the 1 mole equiv. of ozone reactions we have accounted for about 90% of the starting benzaldehyde, we have, on the other hand, accounted for only about 25% of the oxygen atoms of the ozone consumed in the reaction. Perhaps the oxygen unaccounted for reacted with radicals produced from the solvent by the attack of radicals such as XII, XIII, XIV, XV, XVI, and XIX. The exact source of the molecular oxygen evolved during the ozonations also is in doubt. It could arise from intermediate X *via* route 2, from decomposition of the benzoylperoxy radical (XIII), or from reaction of ozone with radicals such as XIII or XVI or perbenzoic acid (XVII). Barnard[21] has shown that ozone reacts with hydroperoxides and peroxy radicals to produce molecular oxygen. The true yield of molecular oxygen may be considerably greater than that actually found, since some may have been consumed by interaction with benzoyl radicals (XIV). The molecular oxygen yield increased greatly as more ozone was allowed to react (*cf.* Table I, experiments 1, 9, and 10), as would be expected if it were produced by the attack of ozone on peroxy radicals or on perbenzoic acid. The fact that the combined benzoic acid and perbenzoic acid yields do not increase during ozonation with more than 1 mole equiv. of ozone, and actually decrease when more than 2 mole equiv. of ozone is employed, indicates that some ozonation of the benzene ring occurs under these conditions. Neither we nor Dick[8] have found any evidence for ring attack when 1 mole equiv. or less of ozone is employed. This ozone attack on the benzene ring might also lead to evolution of molecular oxygen, since it has been shown that excessive molecular oxygen is evolved during ozonation of anthracene with more than 1–2 mole equiv. of ozone.[14]

We, like Briner[5] and Dick,[8] have found that some autoxidation occurs when molecular oxygen is present in the ozonation gas. Table II, experiments 1 and 2 (in comparison with each other and with experiments 1 and 2, Table I), shows that the greater the oxygen–ozone ratio, the less the ozone actually consumed, but the greater the perbenzoic acid yield. Also indicative of the autoxidation mechanism is the fact that ozonation of benzaldehyde in carbon tetrachloride solution with ozone–oxygen rather than ozone–nitrogen produced no benzoyl chloride (*cf.* Table II, experiment 3, and Table I, experiment 4). Presumably benzoyl radicals (XIV) re-

TABLE II
OZONATION OF BENZALDEHYDE WITH OZONE–OXYGEN AT 0°

Expt.	Solvent	Work-up procedure[a]	O_3 employed,[b] mole equiv.	Concentration of O_3, vol. %	Perbenzoic acid,[c] mole equiv.	Benzoic acid,[c,d] mole equiv.
1	CH_2Cl_2	A	1	4.5	0.36	0.26
2	CH_2Cl_2	A	0.2	0.3	0.54	0.14
3	CCl_4	A	1	4.5	0.53	0.32

[a] See Experimental section. [b] In CH_2Cl_2 solvent 75–80% of the ozone reacted, whereas in CCl_4 only 55% reacted. The amount of unreacted benzaldehyde was not determined. [c] Yields are given in moles per mole of benzaldehyde started with. [d] The benzoic acid yield recorded is equal to the total benzoic acid yield obtained after reduction minus the perbenzoic acid yield.

---

(20) C. H. Hassall, *Org. Reactions*, **9**, 73 (1957).

(21) D. Barnard, G. P. McSweeney, and J. F. Smith, *Tetrahedron Letters*, **No. 14**, 1 (1960).

acted with molecular oxygen rather than with the solvent.

There is no reason to believe that the actual attack of ozone on benzaldehyde should be different when ozone–oxygen rather than ozone–nitrogen mixtures are employed. We suggest, therefore, that the initiation of autoxidation is not actually by ozone itself, but rather by the radicals produced through decomposition of intermediate X. The high yields of perbenzoic acid obtained by Dick[8] are readily explained by the decomposition of X by route 1 to benzoylperoxy radicals (XIII), followed by abstraction of hydrogen from benzaldehyde, thus initiating the autoxidation mechanism: $\mathrm{XIII} + \mathrm{I} \rightarrow \mathrm{XVII} + \mathrm{XIV} \xrightarrow{O_2} \mathrm{XIII}$, etc. In this way the benzaldehyde is used up before any appreciable oxidation of it to benzoic acid by perbenzoic acid occurs.

Finally, it is worthy of note that the only effect of a reaction temperature decrease on the ozonation of benzaldehyde is to lower the reactivity of the benzaldehyde, as would be expected (Table I *cf.* experiments 1 and 2).

Experimental

The ozonation setup and equipment are described in earlier papers.[13–15,22] Solvents were pure and anhydrous, unless otherwise stated. The aromatic aldehydes were of the highest grade available commercially. Each was freshly distilled before use.

Ozonation of Benzaldehyde with Ozone–Nitrogen.—A solution of 2.12 g. (20 mmoles) of benzaldehyde in 50 ml. of solvent (methylene chloride, chloroform, carbon tetrachloride, or glacial acetic acid) was treated with an ozone–nitrogen mixture[12–15] containing 10, 20, 40, or 60 mmoles of ozone. The temperature was maintained at 0 to 5° for the first three solvents and 25° for glacial acetic acid. The concentration of the ozone in the gas stream varied, as is characteristic with the silica gel method.[13–15] Ozone absorption was essentially quantitative (95–98%) with the methylene chloride and chloroform reaction mixtures until about 2 mole equiv. of ozone had reacted, after which considerable ozone passed into the iodide trap. With the carbon tetrachloride and glacial acetic acid reaction mixtures, the ozone absorption was 80–90% throughout the reaction. The molecular oxygen yield was determined by procedures already described.[13–15]

In some experiments the *perbenzoic acid yield* was determined on the reaction mixture by the infrared technique reported by Dick.[8] Infrared spectra taken at intervals after the ozonation showed a continuous decrease in the concentration of perbenzoic acid (11.35 μ) and benzaldehyde (12.1 μ) and a corresponding increase in the concentration of benzoic acid (8.87 μ). Some of the yield ranges shown in Table I, experiment 1, are probably due to time lapses between the ozonation and determinaton of products.

The outgases during the ozonation of a methylene chloride solution of benzaldehyde were found to contain about 0.4 mole equiv. of carbon dioxide (determined as barium carbonate); a palladium chloride test for carbon monoxide was positive.

The two work-up procedures employed (A and B) are described below and the experimental results are shown in Table I.

Ozonation of benzaldehyde with ozone–oxygen was carried out as usual[14,22] using gas streams containing 0.3 and 4.5% ozone by volume. Ozone absorption was somewhat less complete with ozone–oxygen than with ozone–nitrogen mixtures. Work-up was by procedure A or B and the results are shown in Table II.

Work-Up Procedure A (Reduction).—The ozonation reaction mixture was poured into a mixture of 5 g. of potassium iodide and 5 ml. of acetic acid, and the resulting mixture was allowed to stand at room temperature for 1 hr. The released iodine was titrated with standard thiosulfate solution. The peroxidic oxygen yields determined in this manner were found to correspond with the **perbenzoic acid** yields determined spectrographically (see preceding description) and in some cases this was the sole method used to determine perbenzoic acid. The reduced reaction mixture was diluted with water and extracted with ether, and the ether extract was extracted with sodium bicarbonate solution. Acidification of the bicarbonate extract, extraction with ether, and evaporation of ether gave benzoic acid melting at 117–120°, recrystallized from water, m.p. 121–122°, and identified by mixture melting point or by infrared spectra.

Gas chromatographic analysis of both the unreduced reaction mixture and the neutral fraction after reduction gave near-identical unreacted benzaldehyde and benzene yields (Tables I and II). Celanese ester No. 9 (5%) on Haloport F was used to determine benzaldehyde at a column temperature of 150°, and cross-linked diethylene glycol adipate (LAC-446; 2%) on acid washed Chromosorb P was used to determine benzene at a column temperature of 75°. The gas chromatograph used was an F & M model 500.

Work-Up Procedure B (Thermal Decomposition).—The solvent was removed from the reaction solution at room temperature, leaving a yellow, oily residue. Gentle warming of the residue initiated an exothermic reaction, which caused the residue to crystallize. A faint odor of phenol could be detected, but the gas chromatograph (same column used for benzaldehyde) showed the presence of only a trace.[23] The residue was recrystallized from water to give benzoic acid melting at 121–122°. Gas chromatographic analysis (see preceding description) before and after the heat decomposition showed that an amount of benzaldehyde, approximately equal to the perbenzoic acid present before the heat decomposition, was oxidized during the heat decomposition.

Determination of Benzoyl Chloride From Ozonation of Benzaldehyde in Carbon Tetrachloride with Ozone–Nitrogen.—An infrared spectrum of a freshly ozonized (0°) solution of benzaldehyde in carbon tetrachloride was identical with that of a freshly ozonized solution of benzaldehyde in methylene chloride to which 0.2 mole equiv. of benzoyl chloride had been added, indicating that about 0.2 mole equiv. of benzoyl chloride had been produced during the ozonation in carbon tetrachloride. Other data are given in Table I, experiment 4. In an analogous experiment using ozone–oxygen no benzoyl chloride was found.

Ozonations of Substituted Benzaldehydes.—The ozonations were carried out with ozone–nitrogen in methylene chloride at 0° as described earlier for benzaldehyde. Ozone absorption was quantitative (1 mole equiv.) with **anisaldehyde.** Work-up by procedure A (reductive) gave 0.61 mole equiv. of anisic acid and 0.2 mole equiv. of recovered aldehyde.

Under the same conditions ***p*-nitrobenzaldehyde** reacted sluggishly and ozone continuously passed into the trap. From 1 mole equiv. of ozone employed, only 0.65 mole equiv. reacted. Work-up by procedure B (heat decomposition) gave 0.08 mole equiv. of *p*-nitrobenzaldehyde and 0.174 mole equiv. of unreacted *p*-nitrobenzaldehyde.

Acknowledgment.—The authors are grateful for grants from the Robert A. Welch Foundation and the American Chemical Society Petroleum Research Fund, which made this work possible. They also thank Dr. A. M. Reader and Mr. Abdul Khashab for performing two of the experiments and Dr. J. E. Batterbee for helpful suggestions.

---

(22) P. S. Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956).

(23) In one case the heat decomposition was carried out in the presence of water; the phenol yield increased to 1–2%.