sulfilimine hydrochloride (III). A known sample of III had a melting point of 75–77°.

Potentiometric titration of II with perchloric acid in glacial acetic acid gave an equivalent weight of 118.9 (calcd. 120.2). Only one of the nitrogens in the monomeric unit is thus basic. A molecular weight determination, run with 0.45 g. of II in 10.21 g. of benzene, gave a freezing depression of 1.43° (calcd. mol. wt. 158).

Reaction of II. A. With Hydrochloric Acid: Formation of Iminodiethylsulfilimine Hydrochloride (III).—To 1.79 g. (0.0075 mole) of the chloride-free sublimate in 10 ml. of 2-propanol was added 7 ml. (0.0067 mole) of a 0.96 *N* 2-propanol solution of hydrochloric acid. Ether (20 ml.) precipitated crystals which were filtered and recrystallized from 2-propanol–ether to give a white crystalline solid, m.p. 75–77°. A test for ionic chloride gave 22.3% (calcd. for $C_4H_{13}ClN_2S$: 22.6%).

B. With Ammonium Chloride: Formation of Bis(iminodiethylsulfilimine) Hydrochloride (I).—A sample of the chloride-free solid was dissolved in excess 2-propanol. Ammonium chloride was added and the mixture was heated repeatedly on the steam bath followed by partial vacuum stripping. After cooling, seeding with a known sample of I produced crystals having a melting point of 90–91°. This compound required 92.5% of theoretical equivalent of base in aqueous titration.

Iminodiethylsulfilimine Hydrochloride (III).—A solution of 2.74 g. (0.01 mole) of I in a few milliliters of 2-propanol was treated with 10 ml. (0.0096 mole) of 0.96 *N* hydrochloric acid in 2-propanol. Ether was added to precipitate the product, which was recrystallized from 2-propanol–ether to give colorless crystals of III, m.p. 75–77°. Analysis gave 22.4% ionic chloride (theoretical: 22.6%).

Addition of ammonia into a 2-propanol solution of III precipitated ammonium chloride. No solid could be obtained from the filtrate. It is believed that an equilibrium is present between the free base and the monochloride, and possibly the dichloride, in the presence of ammonia. This mixture then depresses the melting point of II, making the isolation of the solid difficult. The free base (II) is probably present in the largest concentration, since ammonia appears to be a strong enough base to precipitate ammonium chloride from I.

Compound III did not sublime on heating to 85° under 0.1-mm. pressure except when solid sodium methylate was mixed with the crystals beforehand. Under these conditions, II was obtained.

Iminodimethylsulfilimine Hydrochloride (IV).—Gaseous chloramine (1.65 moles) in excess ammonia was treated with 2 l. of 2-propanol containing 31 g. (0.5 mole) of dimethyl sulfide, as described above for diethyl sulfide. The reaction was maintained at room temperature for 45 min. and filtered to remove ammonium chloride. The filtrate then was evaporated to dryness, yielding a viscous residue which slowly crystallized. The melting point was 111–113° (decompn. 172°).

Anal. Calcd. for $C_2H_9ClN_2S$: C, 18.67; H, 7.05; N, 21.78; S, 24.93. Found: C, 18.39; H, 6.53; N, 21.71; S, 25.20.

Iminodi-*n*-butylsulfilimine Hydrochloride (V).—Filtered chloramine (2.9 moles) was bubbled through 146 g. (1 mole) of *n*-butyl sulfide in 1 l. of 2-propanol, as described above. The reaction mixture was filtered, and the filtrate was evaporated under vacuum at room temperature to give a semisolid material. A 20-g. sample (about 0.05 mole) of this material was dissolved in 100 ml. of cold 2-propanol, heated to 45°, and filtered. The clear filtrate was then combined with 40 ml. (0.04 mole) of a 2-propanol solution of hydrochloric acid. Upon cooling, 4.5 g. of flat white plates were obtained. These plates were recrystallized from warm 2-propanol, m.p. 131–132°.

Anal. Calcd. for $C_8H_{21}ClN_2S$: C, 45.15; H, 9.95; Cl, 16.66; N, 13.17; S, 15.07. Found: C, 44.49; H, 9.98; Cl, 16.59; N, 12.71; S, 15.20.

Reaction of Dioctyl Sulfide with Chloramine.—An 81-g. sample (0.32 mole) of dioctyl sulfide dissolved in 244 g. of 2-propanol was treated with 2.25 moles of filtered chloramine at room temperature. The ammonium chloride was filtered from the reaction mixture at room temperature and the filtrate was evaporated under vacuum to give a waxy solid. Attempts to isolate a crystalline product so far have been unsuccessful.

Acknowledgment.—The authors are indebted to J. N. Lomonte, J. L. McClanahan, and G. L. Kearns of W. R. Grace and Company for infrared, nuclear magnetic resonance, and mass spectrographic studies and to H. H. Sisler and G. A. Russell for their valuable comments.

Competing Reactions in the Ozonation of Anthracene

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Evidence is presented that in protolytic solvents anthraquinone is derived from ozonation of anthracene by two different routes. The first requires three mole-equivalents of ozone and the evolution of three mole-equivalents of molecular oxygen. The second involves the 1,4-addition of a single ozone molecule. In non-protolytic solvents, anthraquinone is produced only by the first route. The second route leads to phthalic acid. Phthalic acid is also produced, in both solvent types, *via* a minor competing bond attack on an outer ring. The solvent effect observed is of a different type than originally suggested. A strong ozone concentration effect also exists.

Anthracene (I) was first ozonized in 1907, in chloroform solution, but no identifiable products were obtained.[1] Roitt and Waters[2] obtained anthraquinone (XI) from ozonation of anthracene in acetic anhydride, but they neither reported the yield nor proved that ozone rather than oxygen was the oxidizing agent. Certain aspects of the ozonation of anthracene were discussed in two preliminary communications from this laboratory.[3–5] The first one[3] showed that ozone was the reactant and proposed that the production of anthraquinone involves the 1,4-addition of one mole-equivalent of ozone to the reactive 9- and 10-positions of anthracene. The second communication[4] reported the evolution of molecular oxygen during the ozonation of anthracene and suggested that three mole-equivalents of ozone are required per mole of anthraquinone produced.[6] The second paper[4,5b] also reported a solvent effect which was thought to control the ratio of atom attack (leading to anthraquinone) to bond attack (leading to phthalic acid) of ozone on anthracene.

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[1] E. Molinari, *Ber.*, **40**, 4160 (1907).

[2] I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 3060 (1949).

[3] P. S. Bailey and J. B. Ashton, *J. Org. Chem.*, **22**, 98 (1957).

[4] F. Dobinson and P. S. Bailey, *Chem. Ind.* (London), 632 (1961).

[5] See also: (a) P. S. Bailey, S. S. Bath, and J. B. Ashton, *Advan. Chem. Ser.*, **21**, 143 (1959); (b) P. S. Bailey, paper presented before the Petroleum Division at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962; preprints, Petroleum Division, American Chemical Society, Vol. 7, No. 4, C-151.

[6] P. G. Copeland, R. E. Dean, and D. McNeil [*J. Chem. Soc.*, 3858 (1961)] also report molecular oxygen to be a product of the ozonation of anthracene.

TABLE I

OZONATION OF ANTHRACENE WITH OZONE–NITROGEN

Experiment	Solvent (mixed, v./v.)	Temp., °C.	Anthracene used, mmoles	Anthracene reacted, mmoles	O_3 reacted, mmoles	Ozonation time, min.	O_2 evolved, mmoles	Anthraquinone, mmoles	Anthraquinone,[a] %	O_2–AQ ratio (actual)	O_2–AQ ratio[b] (corrected)	Acidic products[a]	Work-up procedure[c]
1	CCl_4	−18	3.00	1.60	3.0	40	1.8	0.55	34	3.3			B
2	CCl_4	−18	3.00	2.52	6.0	50	3.8	0.60	24	6.3	4.5		B
3	CH_2Cl_2–CH_3OH (9:1)	−30	3.00	1.54	3.0	40		0.57	37				B
4	CH_2Cl_2–CH_3OH (9:1)	−30	10.00	4.37	10.0	100	5.7	1.63	37	3.5			B
5	CH_2Cl_2	−30	3.00	1.68	3.0	90		0.67	40				B
6	CH_2Cl_2	−30	3.00	1.71	3.0	40	2.1	0.67	39.	3.1			B
7	CH_2Cl_2	−30	3.00	2.88	6.0	50	3.6	0.80	28	4.5	3.2		B
8	CH_2Cl_2	0	5.00	2.75	5.7	50	3.7	1.12	41	3.3			B
9	CH_2Cl_2	−30	10.00	3.00	5.0	60	2.7	0.80	27	3.4	2.3		B[d]
10	CH_2Cl_2	−30	10.00	3.14	5.0	100	2.7	1.13	36	2.4		0.22 g. of crude acids; 15% XXXIV, 2% XXXIII	C
11	CH_2Cl_2	−30	10.00	5.49	10.0	100		2.15	39				C
12	CH_2Cl_2	−30	10.00	5.03	10.0	80	6.2	1.88	37	3.3	3.1	0.7 g. of crude acids; 28% XXXIV, 4% XXXIII	C
13	CH_2Cl_2	−30	10.00	8.87	20.0	115	11.7	3.17	36	3.7	3.3	1.01 g. of crude acids; 17% XXXIV, 1% XXXIII	C
14	CH_2Cl_2	−30	10.00	10.00	30.0	175	21.0	3.48	35	6.0	5.3	1.14 g. of crude acids; 38% XXXIV	C
15	gl. HOAc	16	3.00	1.65	3.0	40		0.86	52				B
16	gl. HOAc	15	10.00	5.70	10.0	100	6.8	2.84	50	2.4	2.1[e]		B
17	AcOH–HOH (9:1)	14	3.00	1.60	3.0	40		1.16	73				B
18	AcOH–HOH (9:1)	14	3.00	3.00	7.5	60	4.0	1.90	63	2.1	1.8		A
19	AcOH–HOH (9:1)	14	10.00	5.02	10.0	105	6.3	3.37	67	1.9	1.7[f]	0.321 g. of crude acids; 9% XXXIV, 7% XXXIII	C
20	AcOH–HOH (9:1)	14	10.00	10.00	25.0	150	14.6	6.44	64	2.3	2.0	0.619 g. of crude acids; 18% XXXIV, 1% XXXIII	C

[a] Per cent yields calculated on basis of anthracene reacting. [b] Corrected to moles of oxygen/mole of anthraquinone at highest anthraquinone yield in same solvent (*i.e.*, expt. 1, 5, 17). [c] See Experimental section. [d] This experiment was carried out twice with nearly identical results. [e] Based on maximum anthraquinone yields obtained by oxidative work-up: expt. 37, Table II. [f] In other similar experiments this value ranged from 1.3–1.7.

TABLE II

OZONATION OF ANTHRACENE WITH OZONE–OXYGEN

Experiment	Solvent (mixed, v./v.)	Temp., °C.	Anthracene used, mmoles	Anthracene reacted, mmoles	O_3 reacted, mole-equiv.	O_3 reacted concn., %[a]	Anthraquinone yield, %[b]	Phthalic acid yield, %	Work-up procedure[c]
21	CCl_4	−18	5.00	2.34	1.0	4	20	. . .	B
22	CCl_4	−20	10.00	10.00	3.1–3.7	3–5	11–19[d]	67 crude 38–63 pure[d,j]	A
23	CH_2Cl_2	−30	5.00	2.70	1.0	4	25		B
24	CH_2Cl_2	−30	5.00	2.72	1.0	4	25		B[e]
25	CH_2Cl_2	−30	5.00	2.53	1.0	2	36		B
26	CH_2Cl_2	−78	10.00	10.00	3.7	4	24		A
27	CH_2Cl_2	−30	10.00	10.00	3.5–3.7	4	23–25[d]	72 crude 50–65 pure[d,j]	A
28	CH_2Cl_2	0	10.00	10.00	3.7	4	26–27[d]		A
29	CH_2Cl_2–CH_3OH (9:1)	−30	10.00	10.00	3.5	4	31–32[d]	54–56 crude[d] 42 pure	A
30	CH_2Cl_2–CH_3OH (5:5)	−30	10.00	10.00	3.5	4	32	55 crude 40 pure	A
31	CH_3Cl_3–CH_3OH (5:5)	−30	10.00	10.00	2.8	3–5	40		D
32	CH_2Cl_2–HOAc (9:1)	0	10.00	10.00	3.5	4	32–35[d]	66 crude 46 pure	A
33	CCl_4–HOAc (5:5)	13	10.00	10.00	3+	3–5	41 crude 36 pure	45 crude 19 pure	E
34	CH_2Cl_2–BF_3[f]	−30	6.00	6.00	3+	3–5	64 crude		A
35	*t*-BuOH–HOH (5:5)	15	5.00	1.93	1.2	4	50		B
36	*t*-BuOH–HOH (3:7)	15	10.00	10.00	3.6	3–5	66 crude		F
37	gl. HOAc	14	10.0	10.0	2.6	4	55–58[d]		A
38	gl. HOAc–NaOAc[g]	14	10.0	10.0	2.6	4	53–55[d]		A
39	HOAc–HOH (9:1)	14	10.0	10.0	2.0	4	72		A
40	HOAc–HOH (9:1)	14	10.0	10.0	2.6	4	65–68[d]	22 crude 18 pure	A
41	HOAc–HOH + NaOAc[g]	14	10.0	10.0	2.6	4	65		A
42	HOAc–Ac_2O (9:1)	14	10.0	10.0	2.6	4	55–58[d]		A
43	HOAc–HOF[h] (3:7)	11	10.0	10.0	3+	3–5	64[i]		E
44	HOAc–CH_3OH (5:5)	10	10.0	10.0	3.3	3–5	62		D

[a] Approximate % O_3 by weight in ozone–oxygen stream. [b] Yield based on anthracene reacting. [c] See Experimental section. [d] Results of several experiments. [e] Same as procedure B, except solution was not refluxed before chromatography. [f] Slightly more than one mole of BF_3 etherate per mole of anthracene. [g] Contained 5 g. of sodium acetate in glacial acetic acid or acetic acid–water, 9:1 (v./v.). [h] The formic acid was a 90% solution in water. [i] A 49% yield of anthraquinone precipitated during the ozonation. The rest was obtained during work-up. [j] The higher yields of phthalic acid were obtained by continuous extraction with ether.

The present paper reports the completed study of the ozonation of anthracene (I) in several different solvents (Tables I and II) and presents evidence that aspects of both mechanisms proposed in the preliminary papers[3-5] are involved in the ozonation. Evidence is also presented that the solvent effect is of a different type than originally supposed.

In 90% solutions of acetic acid in water, ozone absorption by anthracene (I) was very nearly quantitative up to 1.5–1.6 mole-equivalents, after which it occurred fairly readily through 2.5–2.6 mole-equivalents. A 30–45% yield of anthraquinone (XI) precipitated during the ozonation. From the peroxidic filtrate could be obtained either additional anthraquinone, *via* an alkaline or thermal work-up, or anthrahydroquinone (IX ⇄ X) by sodium iodide reduction (which does not affect anthraquinone). The anthrahydroquinone (IX) was isolated and identified in the form of its diacetate (XIII).

After the absorption of one or two mole-equivalents of ozone and an alkaline or thermal work-up procedure, the anthraquinone (XI) yield was 67–73%, based on the amount of anthracene reacting (expt. 17, 19, 39). The yield tended to be slightly lower after an oxidative (expt. 19) rather than a thermal and chromatographic (expt. 17) work-up, probably owing to losses from extra manipulations. Neither anthracene nor anthraquinone is affected by alkaline hydrogen peroxide. The other products were from carbon–carbon bond cleavages. From a one-mole-equivalent run (expt. 19) a mixture of 9% phthalic acid (XXXIV) and 7% 2,3-naphthalenedicarboxylic acid (XXXIII) was obtained. The English workers[6] also isolated XXXIII in 6% yield. In order to isolate a single ozonolysis (bond cleavage) product in good yield it was necessary to use 2.5–2.6 mole-equivalents of ozone and the oxidative work-up procedure. Under these conditions the anthraquinone (XI) yield was 63–68% (expt. 18, 20, 40), and an 18–22% yield of phthalic acid (XXXIV) was obtained (expt. 20, 40).

The results were the same whether ozone–oxygen or ozone–nitrogen[7] mixtures were used. Ozone was also shown to be the ozidizing agent, without the aid of molecular oxygen, by passing the usual volume of ozone–oxygen mixture, but with only catalytic amounts of ozone, through the reaction mixture and showing that the ozone–anthracene stoichiometry was similar to that in experiments using normal ozone concentrations.

Using ozone–nitrogen mixtures and our technique described earlier,[8] it was found that approximately

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(7) G. A. Cook, A. D. Kiffer, C. V. Klumpp, A. H. Malik, and L. A. Spence, *Advan. Chem. Ser.*, **21**, 44 (1959).

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

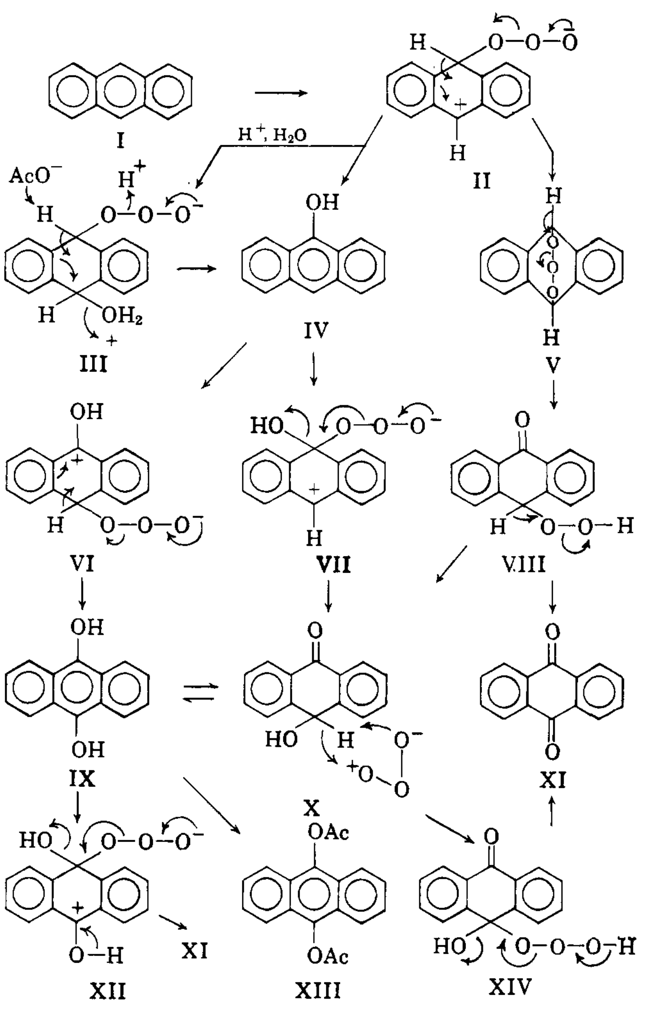
1.3–1.7 moles of molecular oxygen were evolved per mole of anthraquinone (expt. 19) obtained from the one mole-equivalent of ozone runs by the nonoxidative work-up procedure (expt. 17). However, the ratio of molecular oxygen evolved per mole of anthraquinone precipitating during the ozonation was approximately 3.

In nonprotolytic solvents, such as methylene chloride or carbon tetrachloride, ozone absorption was very nearly quantitative up to 2.5–2.8 mole-equivalents of ozone, after which considerable ozone passed into the iodide trap. The best yield of anthraquinone (XI) that resulted from nonprotolytic solvents was 39–41% (expt. 5, 6, 8, 11). This was obtained in methylene chloride solvent, using only one mole-equivalent of ozone from an ozone–nitrogen[8] rather than an ozone–oxygen mixture, chromatographically separating anthraquinone and unreacted anthracene, and calculating the anthraquinone yield on the basis of the anthracene actually used in the reaction. From carbon tetrachloride under the same conditions only a 34% anthraquinone yield was obtained (expt. 1). The anthraquinone could be obtained with or without thermal decomposition and with or without acidic or basic conditions or a chromatographic column, showing that it was directly formed. The molecular oxygen evolved to the anthraquinone obtained ratio was approximately 3[8] (expt. 1, 6, 8, 12). By an oxidative work-up procedure it was shown that the major bond-cleavage product from 0.5 and 1 mole-equivalent of ozone experiments was phthalic acid (XXXIV), along with a small amount of 2,3-naphthalenedicarboxylic acid (XXXIII, expt. 10, 12). Another, unidentified, acid was also found by thin layer chromatography. As more ozone was employed the phthalic acid to naphthalenedicarboxylic acid ratio increased (expt. 13). None of the latter was found when three mole-equivalents of ozone were employed (expt. 14). In these experiments acid yields were low owing, partly, to losses in attempts to isolate all acidic products, and also, probably, to incomplete oxidation of phthalic acid intermediates.

When the reaction was allowed to proceed until 3.0–3.6 mole-equivalents of ozone had been absorbed, in order to ensure completion of bond cleavages in two rings, phthalic acid (XXXIV) was obtained in as high as 67–72% crude and 65% pure yields (expt. 22, 27). It was because of this that it was thought that in nonprotolytic solvents the major ozone attack was at the bonds of lowest bond-localization energy,[9] whereas in protolytic solvents it occurred at the atoms of lowest atom-localization energy.[4,5b,9] For reasons to be discussed, however, it is now apparent that this sort of solvent effect is minor if it exists at all. Also there is no appreciable temperature effect, as shown by comparison of expt. 26–28.

There is a definite ozone-concentration effect with nonprotolytic solvents, but not with protolytic solvents. Whereas, using one mole-equivalent of ozone from ozone–nitrogen mixtures, the anthraquinone yield averaged 40% with methylene chloride solvent (expt. 5, 6, 8), the yield, using one mole-equivalent of ozone from ozone–oxygen and the same solvent and work-up procedure, was only 25% (expt. 23, 24). When two mole-equivalents of ozone were employed from ozone–nitrogen, the anthraquinone yield was only 28% (expt. 7). Similar results were obtained with carbon tetrachloride solvent (expt. 1, 2, 21, 22). It is difficult to estimate the average ozone concentration when ozone–nitrogen mixtures are employed. However, it must be much lower than the roughly 4% used with ozone–oxygen, since expt. 23 and 24 required only about ten minutes and expt. 6 required forty minutes. The same silica gel column was used for the two mole-equivalent of ozone run in expt. 7, but the reaction time was only fifty minutes; thus the ozone concentration in the ozone–nitrogen stream must have been considerably higher than in expt. 6. That these results were actually due to an ozone-concentration effect was proven in two ways. First, when only a 2% ozone–oxygen stream was employed, the anthraquinone yield increased to 36% (expt. 25). When the reaction was carried out in a saturated solution of ozone in methylene chloride at a low temperature, the anthraquinone yield decreased to 18%. Second, the length of the silica gel column for the ozone–nitrogen mixtures was doubled and tripled in expt. 13 and 14 in comparison to 12. Although the reaction time did not double and triple, it at least increased, and the anthraquinone yield was 37–35% in all three experiments. No higher than a 40–41% yield of anthraquinone was ever obtained, even when the ozone-concentration was further decreased (*cf.* expt. 5, 6). No ozone concentration effect was observed with 90% acetic acid solvent (expt. 17, 39).

Scheme I



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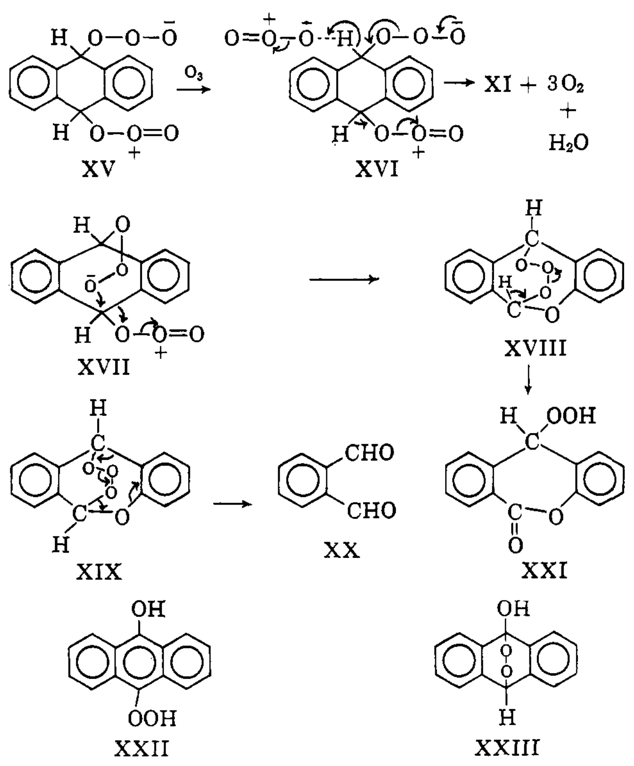
(9) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

It is obvious that the reactions in 90% acetic acid are less complicated than those in nonprotolytic solvents, but that there are, nevertheless, at least two paths to anthraquinone (XI) and also to phthalic acid (XXXIV). It is significant and must be more than coincidental that, using ozone–nitrogen mixtures,[8] three moles of molecular oxygen are evolved per mole of anthraquinone produced, both for the highest yields of anthraquinone obtained using one mole-equivalent of ozone in nonprotolytic solvents and for the anthraquinone which precipitated during the ozonations in 90% acetic acid. It is reasonable to assume, therefore, that the anthracene reacting by this route requires three mole-equivalents of ozone.

Since the center ring is the location of the atoms of lowest atom-localization energy of anthracene, it is reasonable that all reactions of ozone at this ring involve an initial electrophilic attack[9] to give II. There are several possible routes from II to anthraquinone (XI) involving two more mole-equivalents of ozone and the release of three mole-equivalents of molecular oxygen. We believe that the route (or routes) involving IV and IX as intermediates better explains the solvent and ozone-concentration effects. The comparatively clean-cut reactions in 90% acetic acid are due, we believe, to the availability of protons and nucleophilic water molecules, which control the course of the reactions from II to IV as shown in III. Intermediate IV could then undergo an electrophilic ozone attack to give VI, which could react exactly as described for II to give IX. An electrophilic ozone attack on IX should readily give anthraquinone (XI) *via* XII, or the solvent-stabilized form thereof. Alternatively, IV might react with ozone to give VII, which could go on to anthraquinone (XI) *via* intermediate steps such as illustrated by X and XIV; or IV might tautomerize to anthrone, which reacts with two mole-equivalents of ozone to give anthraquinone and two mole-equivalents of molecular oxygen.[10] (See Scheme I.)

In nonprotolytic solvents it is likely that most of the anthraquinone arises by essentially the same route, except that no aid comes from the solvent (*i.e.*, I → II → IV → VI → IX → XII → XI). It is here that we believe the ozone-concentration effect comes into play. The reactions are slower without the aid of protons, but, nevertheless, occur smoothly when the ozone concentration is low. At higher ozone concentrations, however, ozone attacks intermediates II, VI (or VII), and XII nucleophilically, as illustrated in XV, and stops to some degree the reaction course to anthraquinone (XI). This is the mechanism suggested in our second preliminary communication.[4,5b] Intermediate XV could go on over to anthraquinone (XI), but this would require the aid of a third ozone molecule to remove hydride ion as shown in XVI. This should be a slow reaction and, thus, probably occurs to only a minor extent. It is more likely that XV would undergo a rearrangement, as shown in XVII → XVIII, involving cleavage of the central ring and loss of oxygen, and leading eventually to phthalic acid (XXXIV). This 1,2-shift to positive oxygen is analogous to similar shifts in Baeyer–Villiger reactions, which involve the nucleophilic attack of peracids.[11] Possible fates of the rearrangement product are shown by XVIII → XXI and XIX → XX; further rearrangements could occur with XXI, leading directly to products easily convertible to XXXIV during work-up. Such nucleophilic ozone attacks and rearrangements could also occur with intermediates VI (or VII) and XII. In all of these reactions oxygen is a product, which would explain the fact that, as the anthraquinone yield decreased with nonprotolytic solvents, the ratio of molecular oxygen evolved to anthraquinone produced increased (expt. 2, 7, 12, 13, 14), and, at least in the case of carbon tetrachloride solvent, the increase was greater than can be accounted for by assuming that bond attack of ozone, leading to phthalic acid, had occurred with anthraquinone. Further, anthraquinone was shown to be resistant to ozone attack in all solvents. It also does not seem possible that outer ring attack could be occurring with a precursor to anthraquinone, such as IV or IX, since the central ring of these substances should be more reactive toward ozone in reactions leading to anthraquinone than should the central ring of anthracene itself.

SCHEME II



The anthraquinone which does not precipitate during ozonation of anthracene in 90% acetic acid, but is obtained by alkaline or thermal decomposition of a peroxidic intermediate, must have arisen from a reaction involving only one mole-equivalent of ozone and no release of molecular oxygen. Based on an average 1.5 molar ratio of molecular oxygen to total anthraquinone obtained (expt. 19), roughly 50% of the anthraquinone should have arisen by the three mole-equivalent of ozone route and 50% by the one mole-equivalent route. This agrees reasonably well with the amounts isolated, considering the experimental error involved.[8]

The most logical mechanism for the one mole-equivalent of ozone route to anthraquinone involves the completion, II → V, of a 1,4-addition of ozone, as suggested in our first communication.[3,5a] Such an adduct has

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(10) P. S. Bailey and J. E. Batterbee, studies in progress.

(11) C. H. Hassall, *Org. Reactions*, **IX**, 73 (1957).

actually been isolated from ozonation of 9,10-dimethylanthracene, and its structure was proven by n.m.r. spectroscopy.[12] The extent to which such an adduct is produced should be greater with 9,10-dimethylanthracene than with anthracene, owing to activation of the central ring by the methyl groups. Further, it should be more stable in the case of the substituted anthracene.

It is in regard to intermediate V that we believe the principal solvent effect occurs. In the presence of a protolytic solvent, we suggest that V rearranges to VIII, aided by the donation and acceptance of protons by the solvent. Alternative structures to VIII are XXII and XXIII. Intermediate VIII (or its alternatives) then remains in the reaction mixture until alkaline (or strongly acidic) work-up conditions or heat converts it to anthraquinone (XI), reduction converts it to anthrahydroquinone (IX, or its tautomer X), or it is destroyed by excess ozone. Since some phthalic acid was obtained from one mole-equivalent of ozone runs in 90% acetic acid (expt. 19) and since the ozone absorption and oxygen evolution data indicate that this could not have arisen from outer ring attack, intermediate VIII must also undergo rearrangement to some extent as shown by XXIV → XXV. Further oxidation of XXV or XXVI should lead to phthalic acid (XXXIV). Alternatively, the minor cleavage of the central ring could occur at stage V, as will be discussed for reactions in nonprotolytic solvents.

Further evidence for intermediate VIII is as follows. First, the anthrahydroquinone (IX) obtained after the reductive work-up procedure could only have come from reduction of a stable peroxidic intermediate, for had it been produced during the ozonation, it would have been converted to anthraquinone (IX → XII → XI). Second, the easy thermal or alkaline conversion of the peroxide to anthraquinone (work-up procedures A, B, or C) favors VIII, as does also the fact that, when an acetic acid–formic acid mixture was used as solvent, the amount of anthraquinone precipitating during the ozonation increased to 49% (expt. 43). The stronger acid conditions should catalyze the conversion of hydroperoxide VIII to anthraquinone (XI). Third, it is noteworthy that, when only one mole-equivalent of ozone was employed in the 90% acetic acid reactions, the yield of anthraquinone (XI) produced directly was only about 30%, whereas, when 2.0–2.6 mole-equivalents of ozone were employed, this value increased to about 45%; yet, the ratio of molecular oxygen to anthraquinone produced directly was 3 (within experimental error[8]) in both cases. The most logical explanation is that some of hydroperoxide VIII reacted with ozone to give X, followed by X → XIV → XI. This would also result in the evolution of approximately three mole-equivalents of molecular oxygen, since certain hydroperoxides have been reported to react with ozone with release of molecular oxygen, approximately according to the equation $\mathrm{ROOH} + \mathrm{O_3} \rightarrow \mathrm{ROH} + 2\mathrm{O_2}$.[13] Apparently hydroperoxide VIII can also be attacked by ozone at an outer ring, as the 67–73% yields of anthraquinone obtained from the one–two mole-equivalent of ozone reactions in 90% acetic acid (expt. 17, 19, 39) decreased to 63–68% when 2.5–2.6 mole-equivalents of ozone were allowed to react (expt. 18, 20, 40) and to 38% when ten mole-equivalents of ozone were passed through the reaction mixture (glacial acetic acid). In the last instance the phthalic acid (XXXIV) yield increased to 43% (crude). Since anthraquinone (XI) does not react appreciably with ozone under these conditions and since, in the last case, most of the anthraquinone was produced directly, a precursor to XI (presumably VIII or its alternatives) must have been destroyed. In line with this reasoning are the increased ratios of molecular oxygen to total anthraquinone in expt. 18 and 20.

It can be seen from expt. 1, 5, 6, 11, and 12, in which one mole-equivalent of ozone was employed in nonprotolytic solvents, that, after three moles of ozone were used to produce one mole of anthraquinone, the rest of the ozone which reacted was enough to react with only one or two bonds of the remainder of the reacting anthracene. The same conclusion, as will be discussed in greater detail later, can be drawn from expt. 9 and 10 in which only 0.5 mole-equivalent of ozone was employed. Yet the major acidic product obtained from these reactions was phthalic acid (XXXIV), and 2,3-naphthalenedicarboxylic acid (XXXIII) was only a minor product (expt. 10, 12). The inescapable conclusion seems to be that phthalic acid must have arisen from initial attack on the central ring, followed by rearrangement of the product (*e.g.* V or VIII) to a substance which can be oxidized easily to phthalic acid (XXXIV). Since we were unable to get any evidence for intermediate VIII in nonprotolytic solvents by reduction as we did in the acetic acid experiments, we believe that the rearrangement occurs at stage V. It is not surprising that when protons are not available intermediate V undergoes a 1,2-shift to positive oxygen, as indicated by XXVII → XXVIII. Intermediate XXVIII could then undergo the shifts shown to yield XXV ⇄ XXVI, which possibly could be converted to phthalic acid (XXXIV) during the oxidative work-up procedure. Perhaps the unidentified acid found in expt. 12–14 was an incomplete oxidation product of XXVI. Another possible fate of XXVIII is shown in XXIX, whereby phthalaldehydic acid (XXX) is produced directly, along with benzyne. However, no XXX was found after a nonoxidative work-up procedure. (See Scheme III.)

1,4-Transannular ozone additions could also be completed at stages VI, VII, or XII. All of these could go over easily to either anthraquinone (XI) or phthalic acid (XXXIV). However, at stages VII and XII it appears more likely that the indicated reactions would occur before the transannular ozone adduct could form.

Two other observations are worthy of note. First, in expt. 9 where 0.5 mole-equivalent of ozone was employed in methylene chloride solvent, the yield of anthraquinone (XI) was considerably lower than in the corresponding one mole-equivalent of ozone reactions (expt. 5, 6, 8, 11, 12). A careful examination of the data shows that not enough ozone reacted to convert 40% of the reacting anthracene to anthraquinone (XI) by the three mole-equivalent of ozone route and yet bring about conversion of the rest of the reacting anthracene to the precursors of acids XXXIV and XXXIII. Thus, the low yield of anthraquinone (XI) must have been due to the presence of compounds such as IV

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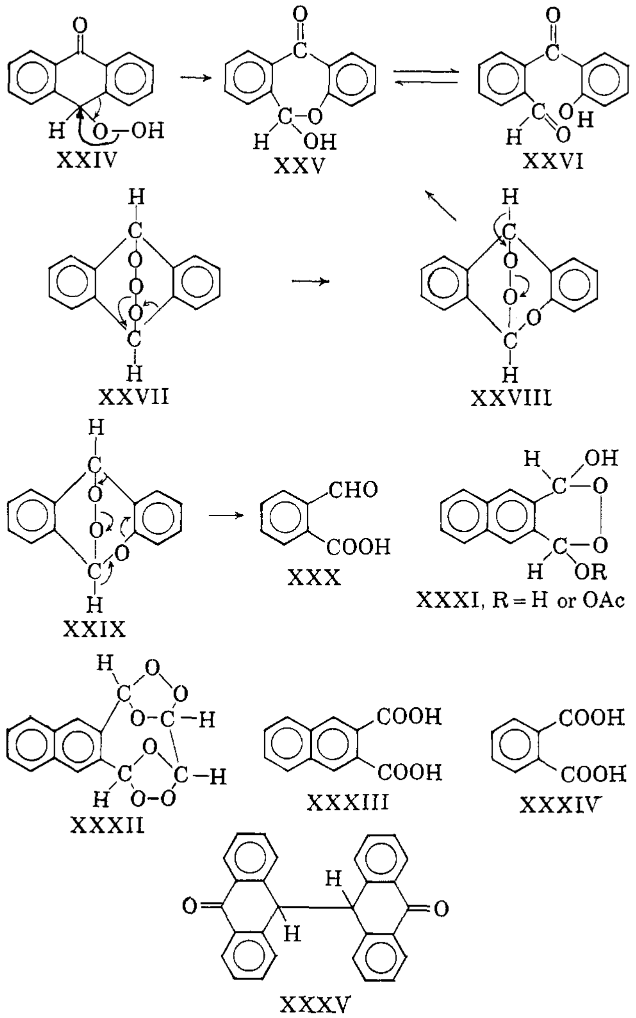
[12] R. E. Erickson, P. S. Bailey, and J. C. Davis, Jr., *Tetrahedron*, **18**, 388 (1962).

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

SCHEME III



and IX in the reaction mixture (*i.e.*, incomplete conversion to XI by the three-mole ozone route). These acidic substances would be expected to remain on the chromatographic column. If one corrects the ratio of molecular oxygen to anthraquinone in expt. 9 (basing it on the 40% anthraquinone yield of expt. 5), the value becomes 2.3, which is in line with the above reasoning. This explanation was verified by expt. 10 where an oxidative work-up procedure was used. Here the anthraquinone (XI) yield increased to 36%, undoubtedly owing to conversion of IV and/or IX to XI during the oxidative work-up. The molecular oxygen to anthraquinone ratio was only 2.4, since only one mole-equivalent of oxygen would be evolved in going to IV and two would be evolved in going to IX during the ozonation.

Second, in one experiment using glacial acetic acid solvent and work-up procedure B, with the exception that the glacial acetic acid mixture was heated during the evaporation of the solvent, the anthraquinone yield fell to 34%, and an 8% yield of bianthrone (XXXV) was isolated along with a small amount of an unknown compound, which might be the methyl acetal of XXV. This furnishes additional evidence for the proposed mechanisms. Presumably, during the heating in glacial acetic acid, an intermediate such as VIII dimerized to bianthrone (XXXV). This is not unreasonable since bianthrone was obtained when a glacial acetic acid solution of 10-bromoanthrone was refluxed.[14] During the heating of the acidic reaction mixture, reactions such as XXIV → XXV must have been promoted, also lowering anthraquinone (XI) yield. No bianthrone (XXXV) was obtained, and the anthraquinone yield was closer to normal (expt. 37) when the reaction was repeated without heating the glacial acetic acid reaction mixture (expt. 16).

It is evident from the foregoing discussion that there is a powerful solvent effect in the ozonation of anthracene, but that it involves largely the fates of intermediates from atom attack rather than the competition between atom and bond attack of ozone. As already stated, this effect appears to be principally the result of the degree of protolytic character of the solvent, as is evidenced by the fact that the per cent yield of anthraquinone (XI) increases as the solvent varies from carbon tetrachloride to methylene chloride to glacial acetic acid to aqueous acetic acid (Tables I and II); this is also roughly the order of decreasing molecular oxygen to anthraquinone ratios (Table I). A mixture of glacial acetic acid and methanol gave, with ozone–oxygen, results similar to those from aqueous acetic acid (*cf.* expt. 40, 44). The patent literature reports a 72% anthraquinone yield from aqueous *t*-butyl alcohol solvent.[15] We were not able to duplicate this (expt. 35, 36), but this may be due to solubility difficulties; the patent used an anthracene–phenanthrene mixture.

The greater yield of anthraquinone (XI) from methylene chloride than from carbon tetrachloride reaction mixtures may be due to either or both the greater protolytic character of methylene chloride or the fact that methylene chloride reacts slightly with ozone to produce small amounts of hydrogen chloride.[16] Another factor may be that the greater polarity of methylene chloride simply increases the ease of ionic reactions. The English authors[6] obtained approximately the same yield of anthraquinone in chloroform solution that we did in methylene chloride, using ozone–oxygen.

Also in line with the proposed theory is the good yield of anthraquinone (XI) obtained using as the ozonation solvent a solution of the Lewis acid boron trifluoride in methylene chloride (expt. 34).

It is difficult to say whether or not there is any solvent effect of the type involving competition between atom and bond attack of ozone on anthracene, as it is difficult to ascertain how much phthalic acid (XXXIV) came from initial bond attack and how much came from center ring attack followed by rearrangements. The seemingly clean-cut reaction in aqueous acetic acid to give nearly 75% anthraquinone (XI) would appear to indicate that 25% initial bond attack occurs. Further, the 2.5–2.6 mole-equivalents of ozone required to complete the reaction fits in well with the 40–45% anthraquinone yield requiring three mole-equivalents of ozone, the 30–35% anthraquinone yield requiring one mole-equivalent of ozone, and 25% bond attack requiring four mole-equivalents of ozone (the fact that more ozone is required with nonprotolytic solvents is probably due to the fact that more intermediates such as XXVI are produced and react further with ozone).

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[14] W. Tadrost and A. B. Sakla, *J. Chem. Soc.*, 3210 (1957).

[15] M. G. Sturrock, E. L. Cline, and K. R. Robinson, U. S. Patent 2,898,350 (Aug. 4, 1959).

[16] G. Slomp, Jr., *J. Org. Chem.*, **22**, 1277 (1957).

By analogy to the ozonation of the 9,10-dihaloanthracenes, where the acid products from bond attack are different from those from rearrangement of atom-attack products, it is possible that a solvent effect involving atom *vs.* bond attack is occurring in the present case also to a small extent.[17] However, this type of solvent effect appears to be dependent on the nucleophilicity of the solvent, and methylene chloride–methanol was as good as or better than aqueous acetic acid for quinone formation.[17] This is not true in the case of anthracene. The yields of anthraquinone were not significantly different from mixtures of methylene chloride, chloroform, or carbon tetrachloride and methanol or glacial acetic acid than from methylene chloride or carbon tetrachloride alone (*cf.* expt. 3, 5, 16, 27, 29–33). Further, the anthraquinone yield was not increased by the addition of sodium acetate to either glacial or aqueous acetic acid (expt. 38, 41). Thus, it appears that the solvent effect involving the competition between bond and atom ozone attack is relatively unimportant. Since neither we nor the English authors have isolated greater than 8% yields of 2,3-naphthalenedicarboxylic acid (XXXIII) from ozonations of anthracene with one–two mole-equivalents of ozone in either protolytic or nonprotolytic solvents, or when only 0.5 mole-equivalent of ozone was employed (expt. 10), this may be close to the extent to which initial bond attack occurs in either type of solvent.

Whatever the extent of the initial bond attack, it apparently involves first the outer ring and then the central ring of anthracene, predominantly, since the only acidic product isolated after complete ozonolysis and a strong oxidative work-up was phthalic acid (XXXIV), expt. 22, 27, 40). This must mean that ozone attack at the outer ring involves a diozonide (*e.g.*, XXXII, as also found with naphthalene[18]) with nonprotolytic solvents, and either XXXI or a mixture of XXXI and XXXII[19] from 90% acetic acid. Upon oxidative work-up, XXXI and XXXII would be converted to 2,3-naphthalenedicarboxylic acid (XXXIII). Further ozonolysis should occur at the original central ring, due to the activating influences of the groups attached, to give, after oxidative work-up, phthalic acid (XXXIV). In contrast, the major bond-attack reactions are at the outer rings of the 9,10-dihaloanthracenes, owing to deactivation by the halogens.[17]

Badger[20] has suggested that the production of anthraquinone during ozonation of anthracene in acetic acid is due to reaction between ozone and acetic acid to give peracetic acid and the attack of the latter on anthracene. At that time he did not know that anthraquinone is also produced in other solvents. Such an explanation is highly unlikely, also, because ozone absorption in acetic acid solutions of anthracene is rapid, whereas we and others[21] have shown that ozone does not react with acetic acid appreciably under ordinary conditions.

Thus it appears that, regardless of solvent, Moriconi[22] was correct in placing anthracene in the group of polycyclic aromatic hydrocarbons which are attacked by ozone predominantly at the atoms of lowest atom-localization energy rather than at the bonds of lowest bond-localization energy. Whether or not his theoretical correlations with oxidation–reduction potentials are meaningful, or merely fortuitous, however, remains to be seen.

Experimental

The ozonation set-up and equipment are described in earlier publications.[8,23] In several cases the ozonation and cooling vessels were placed over a magnetic stirrer, so that the ozonation mixture containing undissolved anthracene and/or products could be stirred. Solvents were pure and anhydrous, unless otherwise stated. The anthracene was usually Matheson's blue-violet fluorescence grade and was dried before use. Where lesser grades were used, the anthracene was purified by chromatography over alumina, m.p. 213° (uncor.).

Ozonation of Anthracene (I).—Several different work-up procedures were used as described below. The results are shown in Tables I and II.

Work-Up Procedure A.—In these experiments a mixture of 3–10 mmoles of finely powdered anthracene in 70–100 ml. of solvent was heated until as much anthracene as possible dissolved, after which the mixture was cooled to the desired reaction temperature. In most cases an ozone–oxygen stream containing approximately 4% by weight ozone was passed through the reaction mixture, which was stirred magnetically, until the desired amount of ozone had reacted. Ozone absorption was near quantitative until 1.5–1.6 (acetic acid solvents) or 2.5–2.8 mole-equivalents (nonprotolytic solvents) had reacted. Reaction appeared to be complete when 2.5–2.6 (acetic acid solvents) and about 3.5–3.6 mole equivalents (nonprotolytic solvents) of ozone had been absorbed. In acetic acid solutions, anthraquinone precipitated during the ozonation. In nonprotolytic solvents, a white "ozonide" began to precipitate after the absorption of about two mole-equivalents of ozone. After the ozonation, the reaction mixture was swept with nitrogen and the solvent was evaporated under reduced pressure on a rotar. To the yellowish sticky residue was added 10 ml. of ethanol and, slowly, a mixture of 10 ml. of 30% hydrogen peroxide and 60 ml. of 2–3% sodium hydroxide (per 10 mmoles of anthracene). The mixture was heated, with stirring, at 65–70° for 2 hr., after which it was cooled and extracted three to six times with 50–100-ml. portions of methylene chloride and once with ether (50 ml.). The combined extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated to give anthraquinone (XI), crude m.p. 275–278°, recrystallized (ethanol) m.p. 282–283°. Identification was by comparison of infrared spectra and mixture melting point method.

To the alkaline mother liquor plus aqueous washings was added hydrogen peroxide (10 ml. of 30% per 10 mmoles of anthracene), and the resulting mixture was heated over a steam bath for 3 hr., cooled, acidified with hydrochloric acid, saturated with sodium chloride, and either continuously extracted or extracted eight times with 70-ml. portions of ether. The ethereal extract was dried over anhydrous magnesium sulfate and evaporated to a tan sticky solid. The crude solid was triturated for 30 min. with refluxing chloroform (20 ml. for 10-mmole runs), after which the mixture was cooled and filtered, giving crude phthalic acid (XXXIV), m.p. (from complete ozonation runs) 190–195°, recrystallized (ethyl acetate) m.p. 202–203°. Identifications were by the mixture melting point method or comparison of infrared spectra.

Work-Up Procedure B.—In most cases an ozone–nitrogen stream was used (desorbed from a 20-cm. silica gel column[7,8]), and molecular oxygen yields were determined by techniques described previously.[8]

The formula used for the final calculation was mmoles of O_2 = [wt. O_2 graph × % O_2 in standard × cc. of gas per min. × min. run × 273° × mm. pressure/wt. total graph × 100 × temp.

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(17) P. Kolsaker, P. S. Bailey, F. Dobinson, and B. Kumar, *J. Org. Chem.*, in press.

(18) P. S. Bailey, S. S. Bath, F. Dobinson, F. J. Garcia-Sharp, and C. D. Johnson, *ibid.*, **29**, 697 (1964).

(19) Compare with the phenanthrene peroxidic ozonolysis product from acetic acid [P. S. Bailey and S. B. Mainthia, *ibid.*, **23**, 1089 (1958)].

(20) G. M. Badger's statement in the discussion section of A. Albert, G. M. Badger, and C. W Shoppee, "Current Trends in Heterocyclic Chemistry," Academic Press, Inc., New York, N. Y., 1958, pp. 5-6.

(21) (a) F. L. Greenwood, *J. Org. Chem.*, **10**, 414 (1945); (b) H. Paillard and E. Briner, *Helv. Chim. Acta*, **25**, 1528 (1942).

(22) E. J. Moriconi and L. B. Taranko, *J. Org. Chem.*, **28**, 1831 (1963); and preceding papers in the series.

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

(°K.) × 760 mm. × 22.4 ml. per mmole] − mmoles of O_3 reacting in a potassium iodide trap.

Ozone absorption by the reaction mixture was usually quantitative, since the ozone concentrations were low. After ozonation, the solvent (unless it was carbon tetrachloride) was removed under reduced pressure (rotar) at room temperature or below, the residue was taken up in 100 ml. of carbon tetrachloride, and the resulting mixture was refluxed until it was no longer peroxidic (approximately 1 hr.). The carbon tetrachloride solution was cooled and poured onto an alumina column. Elution with petroleum ether (b.p. 35–60°, *ca.* 200–300 ml. per mmole run) gave anthracene upon evaporation (m.p. 210–212°), and elution with methylene chloride (*ca.* 150–200 ml. per mmole run) gave anthraquinone (m.p. 282–283°). Identifications were by the mixture melting point method or comparison of infrared spectra.

Work-up procedure C was a combination of A and B. After the oxidative work-up and methylene chloride extraction, the methylene chloride extract was evaporated and the residue was dissolved in carbon tetrachloride and separated on the alumina column to give anthracene and anthraquinone.

The acid yields were determined by a combination of actual isolation and thin layer chromatography; identifications were by thin layer chromatography (t.l.c.) and comparison of infrared spectra. For thin layer chromatography, 8 × 8 in. glass plates sprayed with silica gel G were used. The best developing solvent was methanol. Even with it, however, 2,3-naphthalenedicarboxylic acid (XXXIII) moved more as an elliptical smear than as a spot; thus, quantitative t.l.c. estimates were made only with phthalic acid (XXXIV). The spray reagent was bromocresol green[24] which gave yellow spots on a blue background with both acids (XXXIII and XXXIV). Quantitative estimates were made by comparisons of the chromatographs of 10 mg. of the unknown mixture and 10 mg. of the pure known compound. The spot areas were measured with a Desaga labeling template. R_f values were not reproducible from plate to plate because of variations in layer thickness; thus, all comparisons with known compounds were made on the same plate. The techniques are illustrated by the following example: expt. 19, Table I.

The ether extract containing the acid fraction from ozonation of 10 mmoles of anthracene with 10 mmoles of ozone in 100 ml. of 90% acetic acid gave 0.3210 g. of a brown gummy solid upon evaporation. The solid was triturated for 10 min. with 40 ml. of refluxing chloroform after which the resulting mixture was allowed to stand overnight, and then filtered to give 0.1365 g. of a tannish solid (precipitate A.). On further standing 0.0200 g. of B was obtained from the chloroform mother liquor. Precipitate B was shown both by infrared spectrum and t.l.c. comparisons to be entirely 2,3-naphthalenedicarboxylic acid (XXXIII) with infrared bands at 5.95, 8.20, 8.79, 9.70, 12.90, 13.22, and 15.10 μ. Both infrared and t.l.c. comparisons with precipitate A showed the presence of both XXXIII and phthalic acid (XXXIV, characteristic infrared bands at 6.00, 9.36, 12.47, 12.59, 14.9 μ). The material was triturated with 15 ml. of hot ethyl acetate, and the resulting mixture was allowed to stand overnight. The precipitate (C) weighed 0.0298 g. and was shown by infrared spectra and t.l.c. comparisons to be entirely the naphthalenedicarboxylic acid (XXXIII). Concentration of the ethyl acetate mother liquor gave precipitate D (0.0134 g.) which was shown by t.l.c. comparison with an equal amount (10 mg.) of phthalic acid (XXXIV) to be a 50:50 mixture of XXXIII and XXXIV; this was verified by infrared spectra comparisons which showed the presence of both acids. The ethyl acetate filtrate was evaporated to dryness, and the residue (0.0891 g.) was crystallized from water, giving 0.0150 g. of precipitate E, which was shown by its infrared spectrum to be 2,3-naphthalenedicarboxylic acid (XXXIII). Evaporation of the water mother liquor and trituration of the residue with chloroform gave 0.0701 g. of precipitate F, which was shown by its infrared spectrum to be phthalic acid. Thus, the total yield of phthalic acid (XXXIV) was 0.0768 g. (0.46 mmole or 9% yield based on anthracene reacting) and the infrared spectrum was identical with that of known sample; crude m.p. 190–195° dec., recrystallization (10% hydrochloric acid) m.p. 205° dec. The total yield of 2,3-naphthalenedicarboxylic acid (XXXIII) was 0.0715 g. (0.33 mmole or 7% yield based on anthracene reacting) and the infrared spectrum was identical with that of known sample; crude m.p. 212–225° dec., recrystallization (aqueous ethanol) m.p. 242–243° dec.[25]

The original chloroform mother liquor was shown by infrared spectra and t.l.c. comparisons to contain no more phthalic acid (XXXIV) or 2,3-naphthalenedicarboxylic acid (XXXIII). There was, however, at least one other acid present, which could not be obtained pure enough for identification. This was also true with the methylene chloride reaction mixtures (expt. 10, 12–14), although the acids in the two solvent types did not appear to be the same.

Work-up procedure D was the same as A except that the oxidizing solution consisted of 2 ml. of 30% hydrogen peroxide and 10 ml. of 90% formic acid (for 10 mmoles of anthracene), and the anthraquinone (XI) was filtered from the cooled oxidation mixture.

Work-Up Procedure E.—Anthraquinone (XI) was filtered from the reaction mixture, after which 10 ml. of 30% hydrogen peroxide and 5 ml. of 90% formic acid (per 10 mmoles of I) were added to the filtrate, and the resulting solution was refluxed from 2–8 hr. Anthraquinone was again filtered off, and the filtrate was evaporated to dryness. The residue was treated with 10% sodium hydroxide solution, and anthraquinone was filtered off. The crude anthraquinone melted at 264–286°; it was recrystallized from acetic acid, m.p. 285–286°, and identified by mixture melting point. Phthalic acid (XXXIV) was obtained from the alkaline filtrate as in procedure A.

With **work-up procedure F,** the anthraquinone (XI) was filtered directly from the *t*-butyl alcohol–water ozonation mixture.

Reductive Work-Up to Give Anthrahydroquinone (IX $\rightleftarrows$ X). Ratio of Molecular Oxygen Released to Anthraquinone (XI) Produced Directly. A. Anthrahydroquinone Diacetate (XIII).—The ozonation was carried out as usual with 5 mmoles of anthracene and 10 mmoles of ozone (from an ozone–oxygen stream) in 70 ml. of 90% acetic acid. The reaction mixture was cooled in an ice bath and reduced with sodium iodide. The liberated iodine was reduced with standard sodium thiosulfate; 0.0052 g.-atom of active oxygen was indicated. The precipitate in the reaction mixture was filtered off, dissolved in carbon tetrachloride, and chromatographed as in procedure B, yielding 0.47 g. (2.26 mmoles, 45% yield) of anthraquinone (XI). Based on the molecular oxygen yield in expt. 20 (Table I), the ratio of molecular oxygen to anthraquinone directly produced was 3.2. The filtrate was diluted with 800 ml. of cold water, whereupon 0.21 g. (20% yield) of crude anthrahydroquinone (IX $\rightleftarrows$ X) precipitated. The material gave a transient deep red color with sodium hydroxide solution. A solution of the material and 2 g. of anhydrous sodium acetate in 10 ml. of acetic anhydride was heated at 100° in a nitrogen atmosphere for 2 hr. The solution then was cooled and poured into ice–water, whereupon a pale yellow solid precipitated. The material was washed and dried (0.2 g., m.p. 270–271°) and shown to be anthrahydroquinone diacetate (XIII) by a mixture melting point and comparison of infrared spectra with an authentic sample, prepared by reduction of anthraquinone with zinc dust in acetic anhydride–sodium acetate solution.[26] Similar iodide reductions of nonprotolytic solvent ozonation mixtures gave no XIII. Anthraquinone (XI) treated with acetic anhydride–sodium acetate in the absence of zinc dust was recovered unchanged in 98% yield.

B. Ozonation with Ozone–Nitrogen.—Five millimoles (0.89 g.) of anthracene in 70 ml. of 90% acetic acid solution was ozonized with 5 mmoles of ozone from ozone–nitrogen[7,8] by the procedure described earlier. From the curve obtained with the oxygen analyzer it was determined that 2.6 mmoles of oxygen were evolved. The reductive work-up of the preceding experiment showed 0.0022 g.-atom of active oxygen and gave 0.42 g. (2.4 mmoles) of anthracene and 0.164 g. (0.79 mmoles, 30% yield based on anthracene reacting) of anthraquinone (XI). The ratio of molecular oxygen to anthraquinone was thus 3.3. The filtrate containing anthrahydroquinone (IX $\rightleftarrows$ X) was diluted with water and oxidized with hydrogen peroxide, giving 0.145 g. (0.7 mmole) of anthraquinone. The total anthraquinone yield (m.p. 282–283°) was low (57%), apparently owing to losses in converting anthrahydroquinone to anthraquinone.

C. Anthraquinone (XI) Precipitating Directly.—A solution of 5 mmoles of anthracene in 100 ml. of 90% acetic acid was ozonized with 2.4 mmoles of ozone from an ozone–oxygen mixture,

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[24] Prepared according to J. G. Kirchner, J. M. Miller, and G. J. Keller, *Anal. Chem.*, **23**, 423 (1951).

[25] M. Freund and K. Fleischer, *Ann.*, **399**, 213 (1913).

[26] C. Liebermann, *Ber.*, **21**, 1172 (1888).

and the precipitated anthraquinone was filtered off; yield 0.41 g. (39%), m.p. 282–284°.

D. Alkaline Decomposition of Peroxidic Intermediate (VIII).—In another experiment the entire acetic acid ozonation reaction mixture was poured into 1500 ml. of water and the mixture of solids was removed by filtration and washed with dilute potassium hydroxide solution. A 71% yield of crude anthraquinone was obtained; it was recrystallized from acetic acid, m.p. 283–284°.

Miscellaneous Ozonations of Anthracene. A. With Catalytic Quantities of Ozone in Acetic Acid.—The usual volume of oxygen–ozone (but containing only 0.2% ozone) was passed through 10 mmoles of anthracene (I) in acetic acid solution. A total of 2 mmoles of ozone reacted and an 86% recovery of anthracene was made.

B. Anthraquinone Produced Directly in Nonprotolytic Solvents.—A solution of anthracene in methylene chloride was ozonized with 2.5 mole-equivalents of ozone in an oxygen mixture. The precipitated "ozonides" were filtered off and the filtrate was evaporated under reduced pressure at room temperature (rotar). The residue (0.82 g. from 0.89 g. of anthracene) was shown by infrared spectra comparison to consist of approximately 40% anthraquinone (XI, carbonyl peak at 5.98 μ). Some unidentified carboxylic acids were also present, none of which were XXXIV, XXXIII, or phthalaldehydic acid (XXX).

C. Ozonation with Large Excess of Ozone in Methylene Chloride.—Methylene chloride (300 ml.) was saturated with ozone at −78°. While the solution was kept saturated by the passage of more ozone–oxygen, a solution of 3 mmoles of anthracene in 60 ml. of methylene chloride was added dropwise to the ozonation mixture. The reaction mixture was worked up by procedure B. The anthraquinone yield was 18%.

D. Overozonation in Acetic Acid Solution.—More than ten mole-equivalents of ozone was passed through an acetic acid–anthracene ozonolysis mixture. After the reaction of 2.6 mole-equivalents of ozone, ozone absorption was very slow. The reaction mixture was worked up by procedure E, giving 38% crude or 35% pure (m.p. 285–286°) anthraquinone (XI), and 43% crude or 39% pure (m.p. 206–208°) phthalic acid (XXXIV). Most of the anthraquinone (30% yield) precipitated during the ozonation.

E. Test for Hydrogen in Exit Gases.—The ozonolysis was carried out as usual with ozone–oxygen in 90% acetic acid solution. The exit gases, after passing through the iodide trap, were led through a drying tower and into a sample gas collector. A sample taken after about 0.6 mole-equivalent of ozone had reacted was shown by its mass spectrum to contain no molecular hydrogen. This shows that the 1.5–2.0-mole ratio of molecular oxygen to anthraquinone was not due to loss of oxygen and hydrogen from XV.

F. Dianthrone (XXXV) from Ozonation of I in Glacial Acetic Acid.—The ozonation was carried out as usual with 10 mmoles of ozone in ozone–nitrogen and 10 mmoles of anthracene (I) in glacial acetic acid. Work-up was by procedure B, except that heat (steam bath) was used to evaporate the ozonation mixture under reduced pressure. From the petroleum ether eluate a 4-mmole recovery of anthracene was obtained. From the methylene chloride eluate pure anthraquinone (XI) was first obtained, after which a mixture shown by infrared spectra comparisons to be approximately 80% dianthrone[27] (XXXV, distinctive bands at 6.02, 7.41, 8.50, 12.70, 13.60, and 14.40 μ) and 20% anthraquinone (XI, distinctive bands at 5.98, 7.79, and 12.40 μ) was obtained. This amounted to a 34% yield of anthraquinone and an 8% yield of dianthrone (XXXV) based on the anthracene reacting. In addition, a small amount of an unknown compound was obtained. Infrared bands at 6.01 and 6.30 μ suggest that a diaryl ketone structure was present. No other characteristic bands for functional groups were present.

Attempted ozonations of anthraquinone (XI) were carried out in methylene chloride at −30° and in 90% acetic acid at 14°, using two mole-equivalents of ozone. Titrations of the iodide trap showed that 86 and 98% of the ozone passed through the reaction mixture unchanged in methylene chloride and acetic acid solvents, respectively. The respective anthraquinone recoveries were 95 and 98%; m.p 282–283°. Identification was by the mixture melting point method

Attempted Oxidation of Anthracene (I) and Anthraquinone (XI) with Alkaline Hydrogen Peroxide.—A mixture of 1 g. of each (I and XI separately) in 20 ml. of 30% hydrogen peroxide and 60 ml. of 2–3% sodium hydroxide solution was heated with stirring over a steam bath for 2 hr., after which the mixture was filtered, and the filtrate was extracted with methylene chloride. The recovery of each (I or XI) was 97–99%; anthracene (I) m.p. 212–213°, anthraquinone (XI) m.p. 282–283°. Identifications were by the mixture melting point method.

Attempted Ozonation of Glacial Acetic Acid.—An ozone–nitrogen stream containing 4.44 mmoles of ozone was passed through glacial acetic acid at 16°. The exit gases passed through the iodide trap and into the oxygen analyzer.[8] Titration of the iodide trap with thiosulfate showed that 4.5 mmoles of ozone had passed through it, and the oxygen analyzer indicated that 4.0 mmoles of oxygen was produced, which is within experimental error.[8] An iodide test on the acetic acid showed only a trace of peroxide.

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(27) E. Barnett and M. Matthews, *J. Chem. Soc.*, 380 (1928).

Ozonation of 9,10-Dihaloanthracenes

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Ozonation of 9,10-dibromoanthracene gave anthraquinone, 1,4-dibromo-2,3-naphthalenedicarboxylic acid, and 3,6-dibromo-1,2,4,5-benzenetetracarboxylic acid (dibromopyromellitic acid). Approximately 2 moles of molecular oxygen was evolved per mole of anthraquinone produced when 2 mole equiv. or less of ozone was used. Bromine was also a product and reacted with ozone when more than 2 mole equiv. was employed. There is a definite, though not so great as originally reported, solvent effect involving the competition between atom and bond attack of ozone. Similar results were obtained with 9,10-dichloroanthracene, except that there was little, if any, solvent effect. Mechanisms are discussed.

A preliminary communication[1] reported the ozonation of 9,10-dibromoanthracene (Ia) to give dibromopyromellitic acid (Xa) as the major product and anthraquinone (VIII) as the minor product from methylene chloride solvent and to give the reverse when the solvent was 90% methylene chloride and 10% methanol. It was considered that this solvent effect of nonprotonic *vs.* protonic solvents determined whether initial bond attack[2] or atom attack[2] of ozone on the polycyclic system predominated. Unfortunately, the

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[1] F. Dobinson and P. S. Bailey, *Tetrahedron Letters*, **No. 13**, 14 (1960).

[2] P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).