Ozonation of Benz[*a*]anthracene

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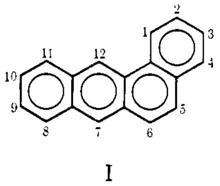
Abstract: The ozonation of benz[*a*]anthracene (I) has been studied in several different solvents. Attack at the bond of lowest bond-localization energy is the major reaction. The data strongly indicate 75% attack at the bond of lowest bond-localization energy to give the expected acid IV and phthalic acid, 15% stepwise attack of 3 equiv of ozone at the atoms of lowest atom-localization energy to give quinone II and molecular oxygen, and 10% addition of ozone at the atoms of lowest *para*-localization energy to give a transannular ozonide which decomposes to II and/or precursors of phthalic acid. A correlation of the three types of attack, based on differences in bond- and atom-, *para*- and bond-, and *para*- and atom-localization energies in a series of polycyclic aromatic hydrocarbons, is made.

During the last several years the ozonations of many important polycyclic aromatic hydrocarbons have been studied.[1-13] In several cases a competition has been observed between attack of ozone at the most reactive bond (to give ozonolysis products) and the most reactive atoms (to give quinones). Moriconi and coworkers[8,9,11,12] have correlated the results of this competition with the corrected redox potentials of the quinone–hydroquinone systems involving the positions in question. They assume a rate-controlling addition of ozone with a transition state having geometry similar to the corresponding dihydro compound and, therefore, predominant ozone attack at the positions of lowest redox potential. Wallenberger[14] has made a similar correlation based on the preferred reaction involving the least loss of resonance energy in the formation of the transition state.

The most thorough study of competing ozone attacks on a polycyclic aromatic compound has been made with anthracene.[7] In this system, ozone was shown to react in three senses, at the bond of lowest bond-localization energy (ozonolysis), at the atoms of lowest atom-localization energy (involving 3 equiv of ozone, release of 3 equiv of molecular oxygen, and the formation of anthraquinone), and at the atoms of lowest *para*-localization energy (to give various center ring attack products *via* a transannular ozonide). The predominant positions of ozone attack were the atoms of lowest atom- and *para*-localization energies.

Moriconi and coworkers[9] were the first to study the ozonation of benz[*a*]anthracene (I). Using 0.5–1.5 mol of ozone per mol of I in methylene chloride–methanol solution, they reported 42–67% yields of 7,12-benz[*a*]anthraquinone (II), based on the amount of I which reacted (unrecovered) during the ozonation. In addition they isolated enough anthraquinone-1,2-dicarboxylic acid (III) to account for 53–74% attack of ozone at the reactive 7 and 12 positions of I, assuming II to be the precursor to III. Although they isolated no product from ozone attack at the most reactive bond of I (the 5,6 bond) they assumed that the amount of I which they did not account for (either in products or by recovery) reacted at this bond. They reported similar results with methylene chloride alone and with carbon tetrachloride, but with glacial acetic acid only a 15% yield of quinone II was obtained. Copeland, *et al*,[5,6] using tetrachloroethane solvent, obtained not only a 17–18% yield of benzanthraquinone (II), but also 15–17% yields



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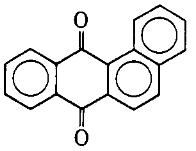
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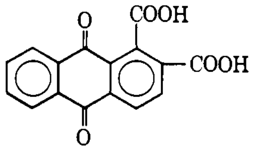
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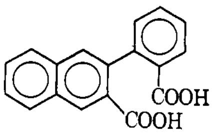
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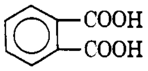
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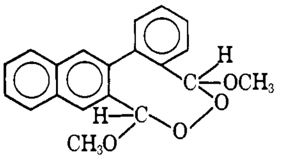
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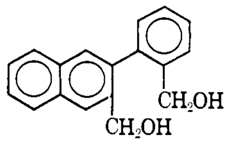
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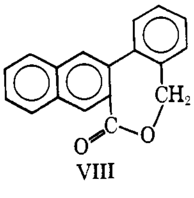
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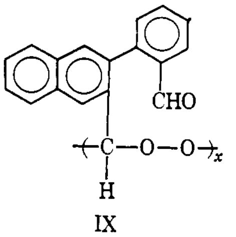
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Table I. Ozonation of Benz[*a*]anthracene (I) in CCl_4 at −15° [a]

	Benz[*a*]anthracene, mmol		Ozone, equiv		Benz[*a*]anthracene-7,12-dione (II)		3-*o*-Carboxyphenyl-2-naphthoic acid (IV)		Phthalic acid (V)						
Expt	Starting	Reacting	Starting[b]	Reacting[c]	mmol	%[d]	mmol	%[d]	mmol	%[e]	Total yield, %[d]	Carrier gas	Molecular oxygen evolved, mmol	O_2/II[f]	O_2/I[g]
1	5.00	2.74	1.0	1.8	0.36	13	1.45	53	1.30	24	90	N_2	2.81	7.8	1.0
2	5.00	4.46	1.8	2.0	0.73	16	2.53	57	1.33	15	88[h]	N_2	5.10	7.0	1.1
3	5.00	5.00	1 8	1 8	0.48	10	2.23	45	1.82	18	73	O_2	...	...	...
4	5.00	5.00	2.0	2.0	0.21	4	2.19	44	1.54	15	63	O_2	...	...	...
5	5.00	5.00	1.8	1.8	0.40[i]	8	*j*	..	*j*	..	..	O_2	...	...	...
6	5.00	5.00	5.1	4.3[k]	0.20[l]	4	None	..	*m*	..	..	O_2	...	...	...
7	10.00	2.61	0.5	1.9	0.33	13	*j*	..	0.51	10[n]	..	N_2	2.95	9.0	1.2
8	5.00	4.76	1.8	1.9	0.54	11	0.12[n]	3	1.00	11	25	N_2	4.50	8.3	0.9
9	5.00	4.83	1.8	1.8	0.30	6	0.27[n]	6	1.80	19	31	O_2	...	....	...

[a] Work-up by oxidative procedure B, unless otherwise stated. [b] Mol passed per mol of starting I. [c] Mol reacting per mol of I reacting. [d] Percentage yield based on amount I reacting [e] Phthalic acid yields are based on 2 mol of phthalic acid per mol of I reacting. [f] Mol of molecular oxygen evolved per mol of II produced. [g] Mol of molecular oxygen evolved per mol of I reacting. [h] The reaction mixture was oxidized with 90% hydrogen peroxide and sodium hydroxide exactly as described for the 30% hydrogen peroxide work-up procedure. [i] In this experiment, the quantities of I recovered and of II produced were determined directly by column chromatography without prior oxidation with alkaline hydrogen peroxide. [j] Quantity not determined in this experiment. [k] The insoluble peroxidic material obtained in this experiment was much less stable than the one obtained with 2.0 equiv of ozone. [l] In this experiment, no II was found; however 0.2 mmol (4%) of anthraquinonedicarboxylic acid (III) was isolated. [m] Substance was shown to be present by tlc, but was not quantitatively determined in this experiment. [n] Low yields, due to milder oxidation conditions. Oxidative work-up procedure A.

of 3-*o*-carboxyphenyl-2-naphthoic acid (IV) from cleavage of the 5,6 bond of I; yields are based on unrecovered I.

The results of Moriconi, *et al.*,[9] fit predictions based on the corrected redox potentials,[8,9,11,12] but not on Wallenberger's resonance energy decrease calculations.[14] Our purpose in restudying the ozonation of benz[*a*]anthracene (I) was severalfold: (1) to account for more starting material in the form of products than was done by the earlier workers; (2) to attempt to determine quantitatively the results of competition among the three modes of ozone attack, as was done with anthracene; (3) to determine whether or not these results and results with other polycyclic aromatics can be correlated with differences in bond- and atom- or bond- and *para*-localization energies in a series of such compounds.

Experimental Section

Equipment and Procedures. The ozonation set-up and procedures, using either ozone–oxygen or ozone–nitrogen, and the method for determining molecular oxygen yields are described in earlier publications.[7,15,16] Column chromatography was done with a 16 × 1 in. Pyrex column using Merck alumina. Tlc experiments employed plates coated with 0.25 mm silica gel G layers prepared with a Desaga/Brinkmann (Westbury, N. Y.) apparatus. The neutral material was chromatographed with methylene chloride, using both ultraviolet light and iodine as detectors. The acidic fractions were chromatographed with a 100:16:12 mixture of 95% ethanol–concentrated ammonium hydroxide–water; detection was with bromocresol green spray reagent which gave yellow spots on a blue background. Melting points were corrected.

Materials. All solvents were pure and anhydrous unless otherwise noted. Benz[*a*]anthracene (Columbia or Baker) usually was pure enough to use as such. Recrystallized (petroleum ether, bp 60–70°) or chromatographed (eluted with 50:50 petroleum ether–benzene), it melted as 159–160°.

Ozonation of Benz[*a*]anthracene (I). General. Solutions or suspension of usually 1.14 g (5.0 mmol) of I in 120–200 ml of carbon tetrachloride, methylene chloride, 3:1 methylene chloride–methanol, methanol, glacial acetic acid, or 90% acetic acid were treated at −30° (methylene chloride and/or methanol), −15° (carbon tetrachloride), or 0–10° (acetic acids) with ozone in either an oxygen (3–6% ozone by weight) or a nitrogen (usually accompanied by a molecular oxygen yield determination, see above) stream. The ozone reacted quantitatively until 1.7–1.9 equiv had reacted. With carbon tetrachloride, methylene chloride, methylene chloride–methanol, and glacial acetic acid this was also the point at which no starting material remained in the reaction mixture (determined by column chromatography as described below). When only 0.5–1.7 equiv of ozone was employed and the unreacted benzanthracene (I) was determined (see below), the ratio of ozone reacting to benzanthracene reacting was still 1.7–1.9. With methanol and 90% acetic acid this ratio was higher (2.4–2.8), probably due to the limited solubility of I in these solvents and, consequently, the greater tendency for initial products (or methanol) than I to react with ozone. When 1.9–4.5 equiv of ozone was passed through the various reaction mixtures, most but not all reacted. When more than 4.5 equiv of ozone was employed, however, most of it passed into the iodide trap. The maximum absorption of ozone was 4.3 equiv. The results of typical experiments with various solvents are shown in Tables I and II.

Ozonation of I in Carbon Tetrachloride. A. The Peroxidic Ozonolysis Product. In typical experiments in carbon tetrachloride (and to a lesser degree in methylene chloride) a straw-colored (apparently due to traces of II) precipitate began to form after 1 mole equiv of ozone had reacted. After ozonation with 1.5–2.0 equiv of ozone, the precipitate was removed by filtration (0.8–0.9 g from 1.14 g of I). By successive concentrations of the filtrate to 10–25 ml, the yield was increased to 1.0–1.5 g. The material melted in the range of 100–115° dec; triturated with methanol, mp 118–124° dec. It slowly decomposed over a period of several days. It released iodine weakly from potassium iodide in glacial acetic acid, but strongly from hydriodic acid. Infrared spectra (Nujol or KBr) showed bands at 3.0 (broad, hydroxyl), 5.9 (intense, carbonyl), and 9.5, 9.6 μ (weak, ether or peroxidic oxygen). The material was either insoluble in or was appreciably decomposed by common solvents. Thus, reliable analyses were not obtained. Treatment of the material with sodium hydroxide or sodium carbonate solutions caused decomposition to intractable oils.

Ozonation in the presence of tetracyanoethylene gave no peroxidic precipitate. However, only tarry or intractable products were obtained, other than the epoxide of tetracyanoethylene.

B. Oxidative Work-up. General Procedure B. The ozonation reaction mixtures were evaporated to dryness under reduced pressure (rotor) and the residue was oxidized with 60 ml of 30% hydrogen peroxide and 60 ml of 10% sodium hydroxide solution (per 5 mmol of I reacting with 1.7–1.9 equiv of ozone; residue about 1.53 g). The vigorous reaction was controlled by first adding 30–50 mg of the solid residue to a stirred solution of 5–10 ml of the hydrogen peroxide and 5–10 of the sodium hydroxide solution, followed consecutively by portions of solid and liquid reactants until all had been employed (3–4 hr). The resulting solution was stirred at room temperature for 3–4 more hr and at 75–85° for at least 7 hr. The reaction mixture was then cooled and ex-

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Table II. Ozonation of Benz[*a*]anthracene in Other Solvents[a]

Expt	Temp, °C	Solvent	Benz[*a*]anthracene, mmol		Ozone, equiv		Benz[*a*]anthracene-7,12-dione (II)		Phthalic acid (V)		Carrier gas	Molecular oxygen evolved, mmol	O_2/II[f]	O_2/I[g]
			Starting	Reacting	Starting[b]	Reacting[c]	mmol	%[d]	mmol	%[e]				
10	−30	CH_2Cl_2	10.00	3.22	0.5	1.6	0.35	11	*h*	..	N_2	3.34	9.6	1.0
11	−30	CH_2Cl_2	5.06	2.66	1.0	1.9	0.24	9	1.05	20	N_2	2.47	10.3	0.9
12	−33	CH_2Cl_2	5.00	2.22	1.1	2.4	0.12	5	0.31	7	O_2	...	...	...
13	−30	CH_2Cl_2	5.00	4.88	1.8	1.9	0.75	15	0.81	8[i]	N_2	5.10	6.8	1.0
14	+10	gl HOAc	10.00	4.84	0.5	1.1	0.71	15	0.59	6	N_2	2.38	3.3	0.5
15	+10	gl HOAc	5.02	4.77	1.8	1.9	0.87	18	1.50	16	N_2	4.90	5.5	1.0
16	+12	gl HOAc	5.00	4.72	1.9	1.9	0.88	19	0.65	7	O_2	...	...	...
17	+10	90% HOAc	10.00	3.08	0.5	1.6	0.49	16	0.87	14	N_2	2.22	4.5	0.7
18	+10	90% HOAc	5.06	2.68	1.0	1.6	0.41	15	0.68	13	N_2	2.10	5.1	0.8
19	+10	90% HOAc	5.06	4.18	1.8	2.1	1.00	24	1.82	22	N_2	4.58	4.6	1.1
20	+10	90% HOAc	5.00	3.08	1.9	2.5	0.40	13	1.90	31	O_2	...	...	...
21	−30	CH_2Cl_2–CH_3OH (3:1)	10.00	2.60	0.5	2.0	0.37	14	0.55	11	N_2	1.55	4.2	0.6
22	−30	CH_2Cl_2–CH_3OH (3:1)	5.02	2.84	1.0	1.8	0.58	20	0.58	10	N_2	2.42	4.2	0.9
23	−20	CH_2Cl_2–CH_3OH (3:1)	5.00	4.36	1.9	2.2	0.62	14	*j*	*j*	N_2	6.77	10.9	1.6
24	−30	CH_3OH	10.00	2.74	0.5	1.9	0.33	12	0.86	16	N_2	1.74	5.3	0.6
25	−20	CH_3OH	6.14	3.48	1.5	2.6	0.62	18	1.24	18	N_2	3.52	5.7	1.0
26	−20	CH_3OH	5.00	3.75	1.9	2.4	0.58	15	1.10	15	N_2	3.40	5.9	0.9

[a] Work-up by oxidative procedure A unless otherwise stated. [b–g] See corresponding footnotes of Table I. [h] Quantity not determined in this experiment. [i] Also obtained 12% IV, 3% of unknown product, probably VIII, and a small amount of an aliphatic acid, probably oxalic acid. [j] In this experiment, 1.58 mmol (36%) of the cyclic peroxide VI was isolated, and the reaction mixture was worked up as described under such isolations.

tracted, first with methylene chloride and then with ether. The combined extracts were evaporated, the residue was dissolved in a minimum quantity (10–15 ml) of benzene, and the resulting solution was chromatographed on the 16 × 1 in. alumina column prepared with petroleum ether (bp 40–80°). The column was first eluted with a 50:50 mixture of petroleum ether and benzene (about 130 ml per mmol of starting I treated with 1 equiv of ozone) to give unreacted benzanthracene (I, mp 158–159°). Next, the column was carefully eluted with benzene (400–600 ml per mmol of starting I) until the yellow band disappeared, after which it was further eluted with 200–400 ml of methylene chloride. The course of the chromatography was followed by tlc (see general procedures above). Evaporation of the benzene–methylene chloride eluate gave **benzanthraquinone** (II); it usually melted around 155–164° and was shown to be 95% pure by infrared spectra comparison with a pure sample (mp 169–170°, characteristic infrared peaks at 5.95 and 6.25 μ) triturated with ligroin, mp 166–168°, further identified by a mixture melting point and tlc R_f value in comparison with the authentic sample. A small, unidentified red band elutable with ethyl acetate remained on the column.

Careful acidification, with stirring, of the dark sodium hydroxide layer with about 15 ml of concentrated hydrochloric acid resulted in much lightening in color and the precipitation of colorless **3-*o*-carboxyphenyl-2-napthoic acid** (IV). Although the melting point was usually low, 210–230° dec in comparison to 250° reported by Copeland, *et al.*,[6] a comparison of its infrared spectrum with that of an authentic sample[17] showed no significant extraneous bands (characteristic bands at 5.9 and 6.35 μ), and only one significant spot was observed with tlc, corresponding with that of the authentic sample; careful recrystallization from ethyl acetate (minimum) and petroleum ether raised the melting point to 250°. The filtrate from separation of IV was extracted with four 200-ml portions of ether (lesser amounts failed to remove all acidic products). Evaporation of these extracts gave phthalic acid (V), usually contaminated with an insignificant amount (about 3% of total) of oxalic acid in the last two extracts. The phthalic acid was identified by its melting point (201–202° after recrystallization from ethyl acetate–petroleum ether), infrared spectrum (characteristic peaks at 6.0 and 6.3 μ), and tlc R_f value in comparison with an authentic sample. The oxalic acid was partially separated through extraction of phthalic acid from the mixture with ethyl acetate and was tentatively identified by its tlc R_f values in comparison with that of an authentic sample. The results of several experiments using the above procedures are shown in Tables I and II.

An oxidative work-up with 90% hydrogen peroxide gave essentially the same results as obtained with 30% hydrogen peroxide and the procedure just described. If not enough time was employed in either case, however, oxidation was incomplete, the yields of acids were low, and much material remained on the column during the quinone (II) and unreacted benzanthracene (I) separations. The benzanthraquinone (II) yield was not appreciably affected, however, whether or not oxidation was complete or whether it was carried out at all. In the latter case, the reaction mixture was filtered and the impure peroxidic precipitate was dissolved in a large volume of ethyl acetate and chromatographed, after which the filtrate was evaporated and the residue was dissolved in benzene and chromatographed, both by the procedure already described. Two-thirds of the yield of II obtained came from the filtrate. It was also shown by infrared spectra and tlc that benzanthraquinone (II) was present in the reaction mixtures before chromatography (characteristic band at 5.95 μ).

In separate experiments benzanthracene (I), benzanthraquinone (II), and 3-*o*-carboxyphenyl-2-naphthoic acid (IV) were essentially quantitatively recovered after being subjected to the same oxidative conditions (above) used on the reaction mixtures. Benzanthracene and benzanthraquinone also were quantitatively recovered unchanged from a benzene solution chromatographed on the alumina column.

Ozonation of Benz[*a*]anthracene (I) in the Presence of Methanol. A. Cyclic Peroxide VI. In a typical experiment using 3:1 methylene chloride–methanol and 1.9 equiv of ozone in nitrogen carrier, the reaction mixture was evaporated to near dryness under reduced pressure (rotor), 20 ml of methanol was added, and the resulting mixture was cooled and filtered. A 32% yield of crude VI melting at 159–165° was obtained, recrystallized from benzene–petroleum ether, mp 178–179°. The material oxidized potassium iodide slowly. Its infrared spectrum was similar to that of the cyclic peroxide from ozonolysis of phenanthrene in methanol[15a] showing neither hydroxyl nor carbonyl bands, but two strong ether bands at 9.19 and 8.95 μ.

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.62; methoxyl, 19.25; mol wt, 322. Found: C, 74.65; H, 5.70; methoxyl, 18.95; mol wt, 322 (mass spectroscopy), 316 (ebulliscopic).

In some cases, the filtrate from the separation of cyclic peroxide VI was evaporated, and the residue was dissolved in benzene and chromatographed as described for the carbon tetrachloride experiments (*e.g.*, expt 23, Table II). In other cases the reaction mixture was worked up by oxidative procedure A (below) without isolating peroxide VI.

The peroxide was shown to decompose on an acidic alumina column as well as often in boiling methanol. It was difficult

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(17) Kindly supplied by Dr. R. E. Dean, Coal Tar Research Association, Leeds, England.

to oxidize. After treatment with a refluxing solution of 10% sodium hydroxide and 30% hydrogen peroxide overnight, a yellow solid was isolated in about 35% yield after acidification, extraction with ether, evaporation, and crystallization and recrystallization from ethyl acetate–petroleum ether, mp 203–205°. The infrared spectrum showed it to be an acid (3.45 μ), but different from IV. Elemental analyses suggest the aldehyde acid corresponding to IV.

Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38; mol wt, 276. Found: C, 77.7; H, 4.8; mol wt 276 (mass spectroscopy).

B. Reductive Work-up. 2-(Hydroxymethyl)-3-[*o*-(hydroxylmethyl)phenyl]naphthalene (VII). The ozonation was carried out as described in the preceding experiment with 10 mmol of I, after which the reaction mixture was evaporated to dryness and the resulting residue was suspended in 100 ml of anhydrous ether. The suspension was added dropwise and with stirring to an ice-cold suspension of 2 g of lithium aluminum hydride in 100 ml of anhydrous ether under an atmosphere of nitrogen. The reaction mixture was stirred for 24 hr at room temperature. Excess lithium aluminum hydride was destroyed by addition of ethyl acetate and dilute sulfuric acid, after which the ether layer was washed, dried, and concentrated. First, a small amount (0.06 g) of material crystallized which melted at 241–243° (recrystallized ether) and appeared to be a ketone (infrared spectrum).

Anal. Found: C, 85.4; H, 6.4; mol wt (mass spectroscopy), 245.

Upon further evaporation (to 15 ml) the dialcohol VII crystallized and melted at 135–137°; recrystallized from ether, mp 142°. The infrared spectrum included peaks at 3.1 (hydroxyl) and 6.25 μ (aryl).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10; mol wt, 264. Found: C, 81.70; H, 6.10; mol wt, 260 (ebulliscopic).

After complete evaporation and treatment of the residue with methanol, a 6.5% recovery of I was obtained. The yield of VII, based on the amount of I reacting, was 23%.

The dialcohol was also obtained *via* a similar lithium aluminum hydride reduction of peroxide VI.

Ozonation of I in Other Solvents. General Oxidative Work-up. Procedure A. The ozonations were carried out as described in the general ozonation procedure. The reaction mixtures were evaporated to dryness under reduced pressure (rotor), and the residues were dissolved in chloroform or methylene chloride (20 ml) and methanol (20 ml), after which 10% sodium hydroxide (20 ml) and 30% hydrogen peroxide (20 ml) were added. The resulting mixtures were refluxed for 12 hr (quantities used were for a 5-mmol run). The reaction mixture was then extracted with methylene chloride and the organic and aqueous layers were worked up as described in the carbon tetrachloride experiments (work-up procedure B). This procedure was used before it was realized that oxidation was incomplete unless the residue and the oxidant came into direct contact.

In several instances the residue from evaporation of the ether layer, after work-up of the basic aqueous layer above, was treated with ethyl acetate, whereupon a new substance melting at 229–230° crystallized. It showed infrared peaks at 5.85 (carbonyl) and 6.25 μ (aryl). Although it originally came from the sodium hydroxide solution, it did not redissolve in base. Its elemental analyses indicate either the dialdehyde corresponding to IV or a lactone (*e.g.*, VIII) produced by a Cannizarro reaction of the dialdehyde to give an alcohol acid, followed by lactonization.

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65; mol wt, 260. Found: C, 82.3; H, 4.9; mol wt (mass spectroscopy), 261 ± 1.

1,2-Anthraquinonedicarboxylic acid (III) was isolated in 4–10% yields in reactions in which excess (4–5 equiv) of ozone was employed, and the reaction mixtures were worked up by oxidative procedures A or B. The material precipitated upon acidification of the sodium hydroxide solution and melted above 300°. It was identified by comparison of its infrared spectrum with that of an authentic sample.[9]

Results

Ozonations of benz[*a*]anthracene (I) were carried out in several different solvents. The results from typical experiments are shown in Tables I and II. With the exception of the runs in methanol and 90% acetic acid, in which I was only slightly soluble, 1.8–1.9 mol of ozone per mol of I reacting was absorbed essentially from the beginning of the ozonation and until all of I had reacted.

In the case of the carbon tetrachloride and methylene chloride reaction mixtures a peroxidic precipitate, contaminated with benzanthraquinone (II) and possibly other products, formed early in the reaction. The precipitate was greater (less soluble) and appeared to be more stable in the carbon tetrachloride reaction. It resisted purification and, therefore, rigorous characterization because it either was too insoluble in, or decomposed in, all common solvents. Judging from its infrared spectrum, which included a strong, broad carbonyl band at 5.9 μ, it is thought to be a polymeric peroxide of type IX rather than a polymeric ozonide as obtained from ozonolysis of phenanthrene;[3] the latter had only a weak carbonyl band in its infrared spectrum. As will be discussed later, the peroxide was oxidized to 3-*o*-carboxyphenyl-2-naphthoic acid (IV) in good yield.

Ozonation in methanol or methylene chloride–methanol produced, in yields as high as 36%, a stable peroxide characterized as VI by its elemental analyses and infrared spectrum, which closely resembled that of the analogous compound obtained from ozonolysis of phenanthrene in methanol.[15a]

In the early stages of the research the reaction mixtures were worked up by oxidation with alkaline hydrogen peroxide in the presence of methanol and either chloroform or methylene chloride (work-up procedure A). The results, shown in Tables II and I (experiments 8 and 9), were comparable to those of Copeland, *et al.*[5] In an effort to obtain a better accounting of starting material, oxidations of the peroxidic residue from evaporation of the carbon tetrachloride reaction mixtures were carried out in the absence of solvent (work-up procedure B). The results, as seen in Table I (especially experiments 1 and 2), were much better, the main difference being in yields of the carboxyphenylnaphthoic acid IV (*cf.* experiments 1 and 2 with experiments 8 and 9). The benzanthraquinone (II) yields, however, did not vary much with the work-up procedure, and for this reason ozonations in other solvents and the resulting tedious isolations were not repeated using the new work-up procedure. In fact, it was shown that II was present before the oxidative work-up.

There appears to be a solvent effect in regard to the benzanthraquinone (II) yields, though not nearly so great as found with anthracene.[7] The maximum yields of II in carbon tetrachloride (or methylene chloride), glacial acetic acid, methanol (or methylene chloride–methanol), and 90% acetic acid were 16, 19, 20, and 24%, respectively. As with anthracene,[7] the yield of quinone was often considerably lower when oxygen rather than nitrogen was the carrier for the ozone. This was supposed to be an ozone concentration effect in the anthracene work. In the present work the yields of all isolated products were less with oxygen carrier, suggesting a competing attack by oxygen leading to different products.

Molecular oxygen was a product, as was also found with the ozonation of anthracene.[7] The ratio of molecular oxygen evolved to benzanthraquinone produced was much higher (7–10 in carbon tetrachloride or methylene chloride), however, than with anthracene. In fact, approximately 1 mol was evolved per mol of benzanthracene (I) reacting.

The maximum yields of benzanthraquinone (II), the carboxyphenylnaphthoic acid IV, and phthalic acid

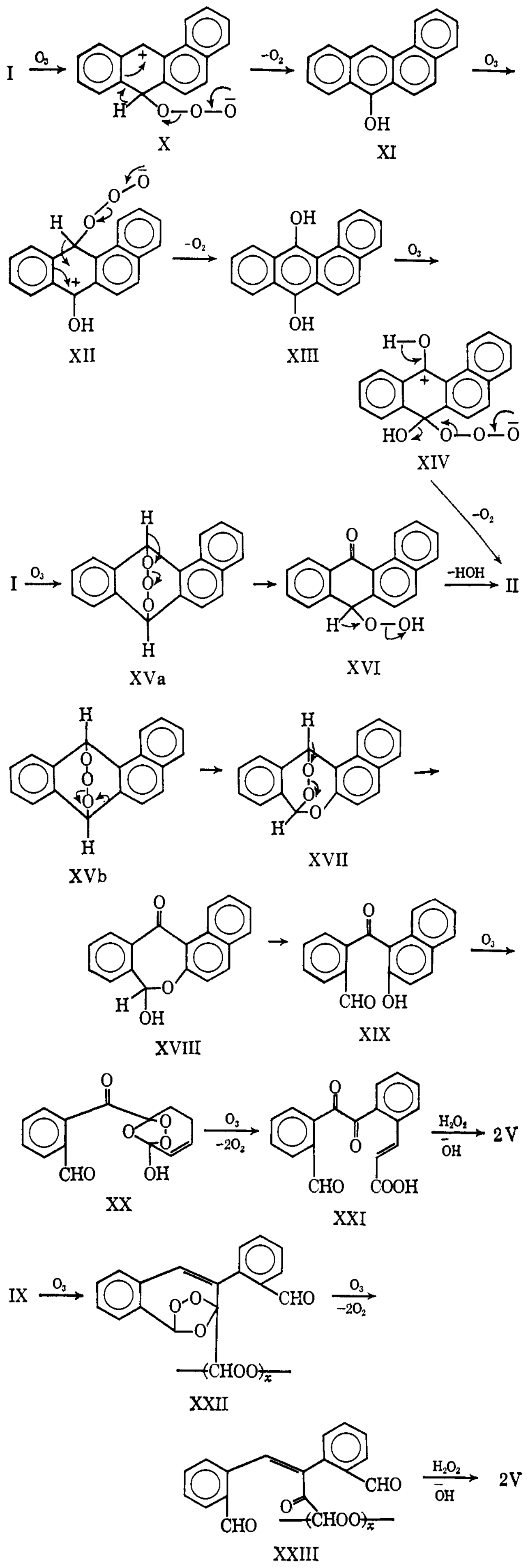
(V) obtained in carbon tetrachloride with ozone–nitrogen were 16, 57, and 24%, respectively, accounting for 97% of the benzanthracene reacting. The yield of phthalic acid was based on an expected 2 mol per mol of I reacting. These results are quite different from those reported by either Moriconi, *et al.*,[9] or Copeland, *et al.*[5] The low yields of IV obtained in the earlier work appear to be due largely to incomplete oxidations of peroxidic ozonolysis products. In the course of our studies using the milder oxidative work-up, partial oxidation products such as VIII and the aldehyde acid corresponding to IV were isolated, and it was noted that much material was lost on the column during chromatography of the neutral fractions after removal of the acidic material. The high quinone II yields reported by Moriconi, *et al.*,[9] apparently were due to incomplete separations of II from starting material, peroxide VI, and partial oxidation products. Such difficulties were also experienced in the early phases of our work.

A reductive work-up, leading to VII, also was tried, but the results were not as good as those obtained by the vigorous oxidative work-up. The dialcohol VII was characterized by elemental analyses, a molecular weight determination, its infrared spectrum, and by analogy to the oxidation product IV. Attempts to convert the peroxidic ozonolysis product from the carbon tetrachloride reaction to the dialdehyde corresponding to IV, by ozonolysis in the presence of tetracyanoethylene,[18] failed. Only tars were obtained. It appears that the unknown dialdehyde is inherently unstable.

Discussion

Important clues to the identities of the competing reactions in the ozonation of benz[*a*]anthracene (I) came from (1) the stoichiometry of the reaction, which showed constant ratios of 1.8–1.9 for ozone absorbed to I reacting and of approximately 1.0 for molecular oxygen evolved to I reacting, until all of I was consumed, and (2) analogy to anthracene.[7] It is obvious that only 1 equiv of ozone is required to cleave the 5,6 bond of benzanthracene to yield the peroxidic precursor of the carboxyphenylnaphthoic acid (I → IX → IV). By analogy to the ozonation of anthracene in carbon tetrachloride or methylene chloride,[7] 3 mol of ozone should be required to produce 1 mol of benzanthraquinone (II) and 3 mol of oxygen, at least in these same solvents. This is illustrated by I → X → XI → XII → XIII → XIV → II. If one rounds off the maximum percentages of II, IV, and V obtained from the carbon tetrachloride reactions to 15, 60, and 25, it follows that 3 equiv of ozone was required for the production of phthalic acid and, assuming no oxygen evolved in the formation of peroxidic precursors of IV, 2 mol of oxygen was evolved. This is illustrated in Table III.

There are two possible sources of phthalic acid (V) which meet the above requirements. One is from attack of 2 equiv of ozone on precursors of 3-*o*-carboxyphenyl-2-naphthoic acid (IV), such as IX; *e.g.*, IX → XXII → XXIII → V. The other involves attack of 2 equiv of ozone on a rearrangement product of the transannular ozonide of I; *e.g.*, VXb → XVII → XVIII → XIX → XX → XXI → V. A similar sequence of reactions was earlier proposed to explain similar observations during the ozonation of anthracene.[7] The evolution of molec-



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(18) R. Criegee and P. Günther, *Chem. Ber.*, **96**, 1564 (1963).

Table III. Stoichiometry of Ozonation of I in Carbon Tetrachloride

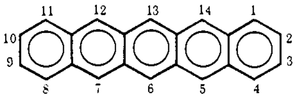
	Benzanthracene (I) consumed, mol	Product	Ozone consumed equiv[a]	Ozone consumed mol	Oxygen evolved equiv[b]	Oxygen evolved mol
	0.15	II	3	0.45	3	0.45
	0.60	IV	1	0.60	0	0.00
	0.25	V	3	0.75	2	0.50
Total	1.00			1.80		0.95

[a] Mol of O_3 required per mol of indicated product. [b] Mol of O_2 evolved per mol of indicated product.

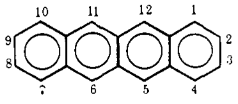
ular oxygen during further ozonation of IX or XIX is not surprising, since hydroperoxides are known to react with ozone in the approximate stoichiometry of ROOH + O_3 → ROH + $2O_2$,[19,20] and it is reasonable that other peroxy types should behave similarly; *e.g.*, $RC^{+}HOO^{-}$ + O_3 → RCHO + $2O_2$. It has been shown previously that stepwise attack on the 1,2 or 3,4 bonds of substituted naphthalenes can occur, as illustrated in XX and XXII.[2]

We believe that the major route to phthalic acid (V) is *via* IX, making it predominantly a product of initial ozone attack on the most reactive bond (5,6) rather than the most reactive atoms (7 and 12) of I. Evidence for this comes from the ozonation of I with 5 equiv of ozone; no 3-*o*-carboxyphenyl-2-naphthoic acid (IV) was isolated, indicating that its precursor IX was destroyed. Furthermore, it appears more likely that the ozone reactions leading to the evolution of oxygen (along with precursors of V) would occur with XXII, which has two peroxy functions, rather than with XX, which has only one. Excess oxygen evolution was not observed in the ozonation of anthracene until 2 equiv or more of ozone had been consumed.[7] Also, oxygen evolution occurred to the extent of only 5–10 mol % with simple naphthalenes.[2]

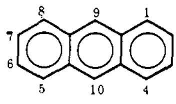
Further insight into the competing reactions occurring during ozonation of benzanthracene (I) and into the source of phthalic acid comes from comparison with the ozonation of anthracene.[7] In 90% acetic acid, a protonic solvent, anthraquinone not only was produced *via* the 3 mol of ozone route (30–40%), as it was also in carbon tetrachloride, but an additional 30–40% of anthraquinone was produced by rearrangement of a transannular ozonide followed by dehydration. In carbon tetrachloride, the transannular ozonide decomposed, instead, to precursors of phthalic acid. In the case of benzanthracene (I) comparable, though less dramatic, results are obtained. In 90% acetic acid, the maximum benzanthraquinone (II) yield was approximately 25% compared to 15% from carbon tetrachloride (and the yields from glacial acetic acid and the methanolic solvents were in between). Thus, this difference, by analogy to anthracene,[7] should represent the yield of the transannular ozonide XV, which in protonic solvents is converted to benzanthraquinone (XVa → XVI → II), but in nonprotonic solvents to precursors of phthalic acid (XVb → XVII → XVIII → XIX).



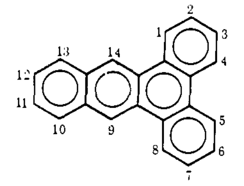
XXIV



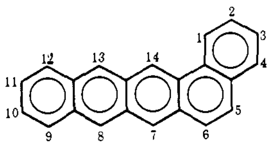
XXV



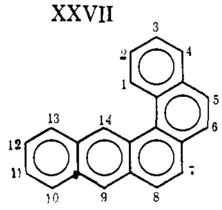
XXVI



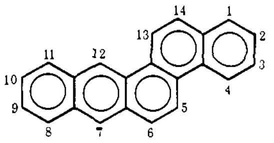
XXVII



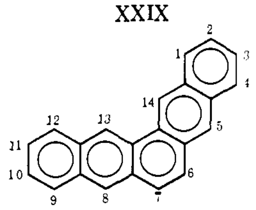
XXVIII



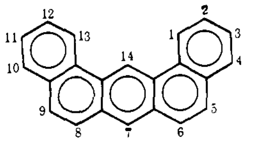
XXIX



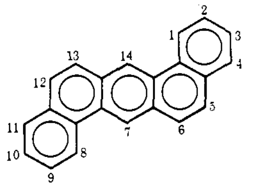
XXX



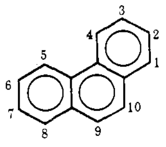
XXXI



XXXII



XXXIII



XXXIV

In summary, the data strongly indicate the following concerning ozonation of benz[*a*]anthracene (I): (1) approximately 25% of the ozone attack occurs at the most reactive atoms (7 and 12) and 75% occurs at the most reactive bond (5,6) of benzanthracene (I); (2) of the 25% attack occurring at the 7 and 12 positions, 15% involves the stepwise attack of 3 mol of ozone per mol of I (at the atoms of lowest atom-localization energy) and the release of 3 equiv of oxygen; the other 10% involves the conjugate addition of 1 equiv of ozone (at the atoms of lowest *para*-localization energy) to give transannular ozonide XV, which in the presence of protonic solvents is converted to benzanthraquinone (II), but in the presence of nonprotonic solvents rearranges to precursors of phthalic acid; (3) of the 75% reaction occurring at the bond of lowest bond-localization energy, about 15% of the product (peroxidic precursor of IV and phthalic acid) reacts with 2 additional equiv of ozone, by the time all of I has been consumed, to give precursors of phthalic acid; the rest remains to be oxidized to the carboxyphenylnaphthoic acid IV.

Admittedly, these conclusions, though reasonable, are based considerably on analogy to anthracene[7] and, thus, are open to some question. It is certain, however,

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

(20) H. Taube and W. C. Bray, *J. Amer. Chem. Soc.*, 62, 3357 (1940).

Table IV. Correlation of Ozonation of Polycyclic Aromatic Hydrocarbons with Localization Energies

Compd	Name	Atom[a]	Nr[a]	La[a]	Bond[b]	Lb[b]	Diene[c]	Lp[c]	Lb–La[d]	Lp–Lb	Lp–La[d]	Predom attack	Ref
XXIV	Pentacene	6	0.80	1.84	1,2	3.18	6,13	3.18	1.34	0.00	1.34	Atom[e]	Not studied
XXV	Naphthacene	5	1.13	1.93	1,2	3.19	5,12	3.25	1.26	0.06	1.32	Atom	8
XXVI	Anthracene	9	1.26	2.01	1,2	3.20	9,10	3.31	1.19	0.11	1.30	Atom *ca.* 75:25	7
XXVII	Dibenz[*a,c*]-anthracene	9	1.50	(2.12)	10,11	3.24	9,14	3.49	(1.12)	0.25	(1.37)	Borderline[e]	Not studied
XXVIII	Benz[*a*]-naphthacene	8	1.09	(1.91)	5,6	3.01	8,13	3.28	(1.10)	0.27	(1.37)	Borderline[e]	Not studied
XXIX	Dibenzo[*b,g*]-phenanthrene	9	1.23	(1.99)	7,8	3.07	9,14	*f*	(1.08)	*f*	*f*	Borderline[e]	Not studied
XXX	Benzo[*b*]-chrysene	7	1.29	(2.02)	5,6	3.08	7,12	3.38	(1.06)	0.30	(1.36)	Borderline[e]	Not studied
I	Benz[*a*]anthracene	7	1.35	2.05	5,6	3.03	7,12	3.41	0.98	0.38	1.36	Bond *ca.* 75:25	Present study
XXXI	Pentaphene	5	1.36	(2.05)	6,7	3.01	5,14	3.45	(0.96)	0.44	(1.40)	Bond	[g]
XXXII	Dibenz[*a,j*]-anthracene	7	1.44	(2.10)	5,6	3.04	7,14	3.51	(0.94)	0.47	(1.41)	Bond	12
XXXIII	Dibenz[*a,h*]-anthracene	7	1.51	2.13	5,6	3.05	7,14	3.51	0.92	0.46	1.38	Bond	11
XXXIV	Phenanthrene	9	1.79	2.30	9,10	3.07	1,4	3.77	0.77	0.70	1.47	Bond	2

[a] Atom of lowest atom-localization energy. Nr = activity number (M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74,** 3357 (1952)). La = atom-localization energy (A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 336, 441). Those numbers in parentheses were estimated from the activity numbers. [b] Bond of lowest bond-localization energy. Lb = bond-localization energy (Streitwieser, footnote *a*, and R. D. Brown, *J. Chem. Soc.* 691, 3249 (1950)). [c] Atoms of lowest *para*-localization energy. Lp = *para*-localization energy (see Streitwieser, footnote *a*, and Brown, footnote *b*). [d] Values in parentheses are due to estimations of La. See footnote *a*. [e] Prediction. [f] Not calculated. [g] E. J. Moriconi and L. Salce, *J. Org. Chem.*, **32,** 2829 (1967).

that more than half (55–60%) of the benzanthracene (I) was attacked at the most reactive bond, and that the ratio of bond to atom attack is greater than one.

As stated in the introduction, one aim of this research was to determine whether or not the competition among the three types of attack of ozone on polycyclic aromatic hydrocarbons of the anthracene (and, possibly, pyrene) type could be correlated with differences in bond- and atom-, bond- and *para*-, etc., localization energies, so that predictions can be made in regard to compounds not yet studied.

In Table IV are listed several polycyclic aromatic hydrocarbons (XXIV–XXXIV) in the order of decreasing differences in bond- and atom-localization energies. Whereas one cannot compare bond- and atom-localization energies directly with each other and draw any conclusions, the differences between these values can be compared. Thus, all compounds studied so far fit, at least qualitatively, the correlation. The present benz[*a*]anthracene results fit in well with both this correlation and the similar correlation of Wallenberger,[14] but not with the less rigorous correlation based on redox potentials. The compounds in between anthracene and benzanthracene (I) would be interesting to study, since one of them could be on the theoretical borderline, giving equal amounts of bond and atom attack products. Further studies also should be made with other compounds of Table IV in order to see how quantitatively the experimental results fit into Table IV.

No distinction is made in Table IV in regard to the two types of attack at the most reactive atoms of the molecule, *e.g.*, whether stepwise oxidation at the atoms of lowest atom-localization energy or concerted addition at the atoms of lowest *para*-localization energy, to give a transannular ozonide. The order of differences between bond- and atom-localization energies is essentially the same as that between *para*- and bond-localization energies. Also included in Table IV are differences in *para*- and atom-localization energies. It should be interesting to investigate experimentally whether or not correlations can be made with these values.

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