Further Studies Concerning the Ozonolysis of Phenanthrene

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This paper presents further information concerning the nature and behavior of the peroxidic products from ozonolysis of phenanthrene in "inert" and in "reactive" solvents.

In earlier papers the ozonolyses of phenanthrene in methanol[1] and in chloroform[2] were reported. The present paper presents the experimental details of the ozonolysis of phenanthrene in chloroform[2] and additional results of ozonolyses both in "reactive" and in "inert" solvents.[3]

Subsequent to our earlier papers in this series, Wibaut and de Boer[4] published a "preliminary communication" in which they assigned to the first isolable product from the ozonolysis of phenanthrene in methanol the cyclic structure (VIa)

a) R = H; b) R = CH₃; c) R = CH₂CH₃
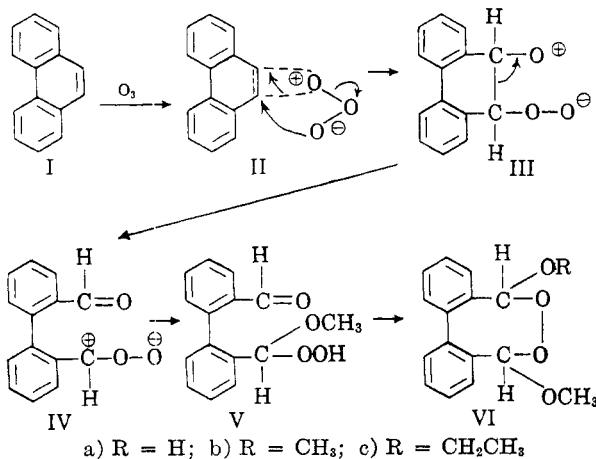
(1) P. S. Bailey, J. Am. Chem. Soc., 78, 3811 (1956).

(2) P. S. Bailey and S. B. Mainthia, J. Org. Chem., 21, 1335 (1956).

(3) The terms "reactive" and "inert" refer to possible reaction of the solvent with the zwitterion intermediate. See reference 1 for details of the Criegee mechanism.

(4) J. P. Wibaut and T. J. de Boer, Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B., 59, 421 (1956).

(5) R. Criegee, H. Pilz, and H. Flygare, Ber., 72, 1799 (1939).

rather than the open-chain structure (V) assigned by us.[1] Our crude product (m.p. 84-88°) showed a positive, though weak, lead tetraacetate test for a hydroperoxide[5] and its infrared spectrum, taken either in solution or in KBr disk, showed strong hydroxyl and carbonyl bands.[1] Wibaut and de Boer[4] were able to obtain a purer product (m.p. 96.5-97.5°) and found that the infrared spectrum taken in Nujol mull showed no carbonyl band.

Repetition of our earlier work leads to the following conclusions. At the end of the ozonolysis the cold methanolic reaction mixture contains high concentrations of V, produced from IV probably via II and III.[6] This is evidenced by a strong lead tetraacetate test for a hydroperoxide.[5] With time and/or increase of temperature the equilibrium shifts toward the more stable and less soluble cyclic tautomer VIa, which can be precipitated by addition of cold water or by cooling a reaction mixture containing a minimum of solvent. At room temperature the acidic nature of V, in equilibrium with VIa, catalyzes the conversion of VIa to the peracetal, VIb.

Both the freshly precipitated VIa (m.p. 86-88°) and that purified to the extent reported by Wibaut and de Boer[4] (m.p. 97-98°) contain V as an impurity; their infrared spectra taken in a Nujol mull still show faint carbonyl bands. The highly purified product (m.p. 116-117°) had no carbonyl band in its infrared spectrum, taken in Nujol. The infrared spectra taken in chloroform or bromoform, however, showed strong carbonyl bands.

Wibaut and de Boer[4] showed that the strong carbonyl bands in the KBr disk spectrum were due

(6) P. S. Bailey, Chem. & Ind. (London), 1148 (1957).

to decomposition. Those in the solution spectra apparently are the result both of decomposition and of equilibrium with V. After a dilute chloroform solution of pure VIa had been irradiated with infrared light for fifteen minutes, the recovered product was pasty and contained 10% less active oxygen.

The fact that crude VIa can be purified by recrystallization from benzene indicates that at least in this solvent the equilibrium between V and VIa lies far in the direction of VIa. This also appears to be true with methanol. Whereas crude VIa in methanol or ethanol was converted to VIb and VIc, respectively,[1] no such reaction was obtained with pure VIa until a drop of hydrochloric acid was added.

The first paper of this series[1] reported the isolation, one time only, of a crystalline material thought to be a cyclic dimer of V. It is now apparent that this material was VIa of approximately the same purity as obtained by Wibaut and de Boer[4]. We were misled by an erroneous molecular weight determination and by the unfortunate circumstance that, this one time, no appreciable decomposition occurred during the observation of the infrared spectrum in a KBr disk. This spectrum is different from those of crude VIa taken in a KBr disk, which showed strong carbonyl bands.[1] It is similar to those of pure VIa taken in a Nujol mull, except that it has a very weak carbonyl band.

As stated in the second paper of this series[2] and as reported also by Wibaut and de Boer,[4] ozonolysis of phenanthrene in chloroform gives a polymer of zwitterion IV, rather than a monomeric mono-ozonide (VII) as reported by Schmitt, Moriconi, and O'Connor.[7] The latter authors were misled by a Rast molecular weight determination (during which decomposition occurred[4]) and the infrared spectrum which showed bands in the 5.7–5.9μ region. These bands, which since have been shown to be due to carbonyl-containing impurities,[8,9] had earlier been reported to be characteristic of ozonides.[10] O'Connor, Schmitt, and Moriconi[11] have acknowledged the misassignment of structure.

Our material (m.p. 139–140°) was obtained from ozonolyses of phenanthrene in chloroform, carbon tetrachloride, 1,2-dichloroethane, or methyl chloride. Molecular weight determinations carried out cryoscopically in various solvents showed it to be at least a hexamer. We have assigned it a poly-

ozonide structure (VIII) on the basis of infrared spectra, which show only a weak carbonyl band and bands at 9.5 and 9.6μ which have been shown to be typical of most simple ozonides.[8] Alternative structures are IX and X. In each of these cases (VIII, IX, or X) the chain could be terminated by the addition of a small molecule such as water. If the material were IX or X, however, the infrared spectrum should show no trace of a carbonyl band. The band at 9.5μ probably is due to the ether linkage of the ozonide ring. Five-membered cyclic ethers have been shown to absorb at 9.1–9.3μ whereas open-chain and cyclic ethers of larger size absorb at 8.6–9.1μ.[12]

Wibaut and de Boer,[4] on the basis of a cryoscopic molecular weight determination in benzene, concluded that their polymer of IV (precipitated from the chloroform ozonolysis reaction mixture by addition of ether, and carefully washed with ether, m.p. 128–129°) was trimeric. As would be expected of a lower molecular weight polymer of structure VIII, a relatively strong carbonyl band was reported in the infrared spectrum[4]. An active oxygen determination indicated that the material was not contaminated with nonperoxidic decomposition products.[4] It seems probable that the ozonolysis product is a mixture of polymers of various lengths and that Wibaut and de Boer[4] concentrated the trimer whereas we concentrated higher polymers. An alternative explanation is that during our recrystallization further polymerization occurred through abstraction of some of the small chain terminating molecules.

It was evident that the material of Schmitt, Moriconi, and O'Connor[7] (m.p. 65–90°) contained both the polymeric ozonide and nonperoxidic ozonolysis products. We were able to obtain a material similar to this only by allowing the ozonolysis reaction mixture to stand before precipitation, or by redissolving the product in chloroform and allowing this solution to stand. In each case the
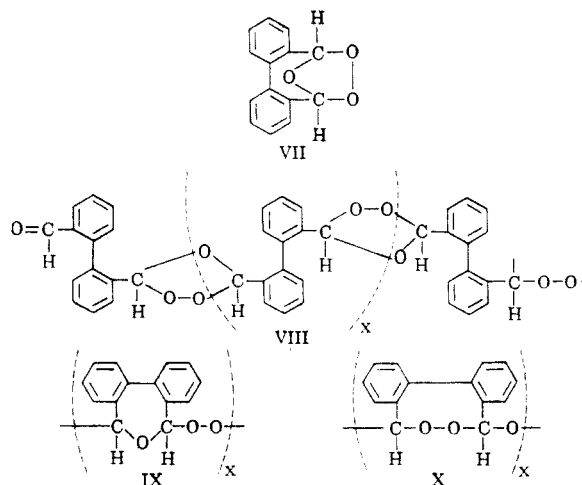
(7) W. J. Schmitt, E. J. Moriconi, and W. F. O'Connor, *J. Am. Chem. Soc.*, **77**, 5640 (1955).

(8) R. Criegee, A. Kerckow, and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955).

(9) E. Briner and E. Dallwigk, *Compt. rend.*, **243**, 630 (1956); *Helv. Chim. Acta*, **39**, 1446 (1956).

(10) E. Briner, *et al.*, *Helv. Chim. Acta*, **35**, 340, 345, 353, 1377 (1952); *Helv. Chim. Acta*, **36**, 1166, 1757 (1953); *Helv. Chim. Acta*, **37**, 620, 1558, 1561 (1954); *Compt. rend.*, **234**, 1932 (1952); *Compt. rend.*, **237**, 504 (1953).

(11) W. F. O'Connor, W. J. Schmitt, and E. J. Moriconi, *Ind. Eng. Chem.*, **49**, 1701 (1957).

(12) G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953).

resulting material was much lower melting, contained much less active oxygen, and showed strong carbonyl bands in its infrared spectrum.

The polymeric ozonide(VIII) was reduced to 2,2'-biphenyldicarboxaldehyde and was oxidized to diphenic acid. The yields were much lower, however, than from the methanol ozonolysis products (VI)[1]. Decomposition of VIII gave a mixture of 2,2'-biphenyldicarboxaldehyde, diphenic acid, 2'-formyl-2-biphenylcarboxylic acid, and an oily phenolic material.

Ozonolysis of phenanthrene in glacial acetic acid gave a material which appears to be a mixture of the polymeric ozonide (VIII) and an acetoxy hydroperoxide (XI).

XI
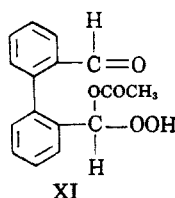
EXPERIMENTAL[13]

The ozonator and techniques used in this research were the same as described in an earlier paper.[14] The phenanthrene was Eastman Kodak Co. White Label 599. The melting point of 99–100° is indicative of its high purity. The methanol was distilled over magnesium methoxide.[15] The chloroform (Baker and Adamson) was carefully purified[16]; the purity of the peroxidic ozonolysis product from chloroform solution was dependent on the purity of the chloroform. All other liquid ozonolysis solvents were carefully dried and redistilled.

Ozonolysis of phenanthrene in methanol to give 3-hydroxy-8-methoxy-4,5,6,7-dibenzo-1,2-dioxacyclooctane (VIa). An ozone-oxygen stream containing 4% ozone by weight was passed at a rate of 40 l. per hour into a suspension of 4.0 g. of phenanthrene in 80 ml. of methanol at −20°, until all of the phenanthrene had dissolved and ozone had begun to pass into the potassium iodide trap. A total of 1.1 moles of ozone per mole of phenanthrene reacted. The dissolved, unreacted ozone was swept out by a stream of dry oxygen. The solution gave a strong lead tetraacetate test for a hydroperoxide.[5] To the cold reaction mixture was added slowly 200 ml. of ice water while the sides of the containing vessel were scratched. The bulky precipitate was filtered, washed, and dried; 4.6 g. (79%), m.p. 86–88°. Trituration with petroleum ether raised the melting point to 97–98°.[17] Both this and the material before trituration gave weak lead tetraacetate tests and had faint carbonyl bands (5.9 μ) in

(13) Melting points are corrected. Microanalyses were performed by the microanalytical laboratory of the University of Texas Biochemical Institute. The active oxygen determinations were done by the method of R. Criegee, G. Blust, and G. Lohaus, *Ann.*, **583**, 4 (1953).

(14) P. S. Bailey and S. S. Bath, *J. Am. Chem. Soc.*, **79**, 3122 (1957).

(15) A. I. Vogel, *A Textbook of Practical Organic Chemistry*, 3rd Ed., Longmans Green and Co., New York, N. Y., 1956, p. 169.

(16) Reference (15), p. 176.

(17) Wibaut and de Boer[4] reported that they triturated with ether to obtain this material. We found, however, that the material partially dissolved and/or became gummy in ether.

their infrared spectra. After several recrystallizations from benzene, the material melted at 116–117°.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46; active O, 6.20; mol. wt., 258. Found: C, 70.25; H, 5.58; active O, 6.01; mol. wt. (cryoscopic in 1,2-dibromoethane) 270.

The pure substance gave a negative lead tetraacetate test, strongly released iodine from sodium iodide solution, was stable to shock, remained undecomposed indefinitely at 0°, but decomposed at room temperature after a few days. Its infrared spectrum taken in a Nujol mull showed a strong hydroxyl band (3.0 μ) but no carbonyl band. The spectra in chloroform or bromoform were quite different and had strong carbonyl bands at 5.9 μ.

When the ozonolysis was repeated just as before, except that 4 g. of phenanthrene in only 50 ml. of methanol was used, and the ozonolysis solution was cooled to −50°, a 34% yield of crude VIa (m.p. 87–89°) precipitated.

Infrared irradiation of a chloroform solution of 3-hydroxy-8-methoxy-4,5,6,7-dibenzo-1,2-dioxacyclooctane (VIa). An approximately 1% solution of pure VIa was irradiated with infrared light for 15 min., after which the solvent was rapidly evaporated under vacuum on a Rinco evaporator. A paste remained.

Anal. Calcd. for $C_{15}H_{14}O_4$: active O, 6.20. Found: active O, 5.4.

In another instance the pasty residue was triturated with petroleum ether. A low recovery of crystals melting at 95–96° was obtained. Similar results were obtained by allowing the chloroform solution to stand for 15 min. without irradiation.

Conversion of 3-hydroxy-8-methoxy-4,5,6,7-dibenzo-1,2-dioxyacyclooctane (VIa) to *3,8-dimethoxy-4,5,6,7-dibenzo-1,2-dioxacyclooctane* (VIb) was accomplished by dissolving 1 g. of pure VIa in 25 ml. of methanol and adding 1 drop of concentrated hydrochloric acid. Precipitation began immediately and was complete in 10 min. A yield of 0.9 g. (85%) of VIb melting at 175–176° was obtained. Identification was by the mixture melting point method.[1] When this was repeated with no hydrochloric acid present no precipitate formed. After several days the solution lost its active oxygen content. Likewise, substitution of a drop of sulfuric acid for hydrochloric acid brought about decomposition rather than conversion to VIb.

Ozonolysis of phenanthrene in methanol to give 3,8-dimethoxy-4,5,6,7-dibenzo-1,2-dioxyacyclooctane (VIb). The ozonolysis was carried out with 2 g. of phenanthrene in 40 ml. of methanol just as described in the first experiment. At the end of the reaction, 4–5 drops of concentrated hydrochloric acid were added. Precipitation began immediately and was complete after 10 min. The yield of VIb melting at 177–178° was 2.5 g. (82%); recrystallized from methyl ethyl ketone, m.p. 180–181°, no depression in melting point in admixture with an authentic sample.[1]

Ozonolysis of phenanthrene in inert solvents to give the polymeric ozonide (VIII). Into a solution of 5.9 g. of phenanthrene and 60 ml. of chloroform cooled to −60° was passed an ozone-oxygen stream, containing 4% by weight ozone, at a rate of 40 l. per hour. The ozone was absorbed quantitatively until one mole per mole of phenanthrene had reacted. Dissolved ozone was swept out with a dry oxygen stream and the reaction mixture was allowed to come to room temperature. Upon addition of ligroin 7.3 g. (97% yield) of material melting at 129–130° precipitated. Similar results were obtained by addition of methanol. Several recrystallizations by dissolving in benzene and reprecipitating with ligroin raised the melting point to 139–140° (77% yield). The material is colorless, amorphous in appearance, stable to shock, releases iodine from sodium iodide solutions, remains undecomposed indefinitely at 0°, but decomposes in a few days at room temperature. Its infrared spectrum taken either in chloroform or in Nujol mull showed a weak carbonyl band (5.9 μ) and very strong twin bands at 9.5 and 9.6 μ.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.5; active O, 7.1; Found: C, 74.58; H, 4.8; active O, 7.0.

Ozonolyses in carbon tetrachloride and 1,2-dichloroethane by the same procedure gave the same product. For the *ozonolysis in methyl chloride*, gaseous methyl chloride was passed through concentrated sulfuric acid, solid sodium hydroxide, and anhydrous calcium chloride and then condensed at −80° in the ozonolysis flask containing the phenanthrene. After the ozonolysis the solvent was allowed to evaporate and the residue was purified as described in the chloroform experiment. The product was identical with those from the other inert solvents.

Cryoscopic molecular weight determinations of polymeric ozonide (VIII). The molecular weight was determined cryoscopically in several solvents. The results varied somewhat in the different solvents, probably because decomposition occurred in varying degrees (see next experiment). In nitrobenzene the molecular weight changed rapidly with time. It appears that the material is at least a hexamer; probably it is of higher molecular weight.

Calcd. for $(C_{14}H_{10}O_3)_x$: x = 9, 2034; x = 6, 1356; x = 5, 1130; x = 3, 678; x = 2, 452; x = 1, 226. Found: 2020, 1860 (bromoform); 1392, 1370, 1350 (benzene); 1250, 1200 (nitrobenzene, quickly); 508 (nitrobenzene, 1 hr.); 268 (nitrobenzene, 2 hr.); 540, 550 (acetophenone, 1-2 hr.).

Decomposition of polymeric ozonide on standing in solution. A solution of the polymeric ozonide in chloroform was allowed to stand for 3 days after which time it was evaporated. The residue melted at 125-127°.

Anal. Calcd. for $(C_{14}H_{10}O_3)6$: active O, 7.1; mol. wt., 1356. Found: active O, 6.4; mol. wt., 416.

A similar solution was allowed to stand for 5 days. The residue melted at 80-90°.

Anal. Calcd. for $C_{14}H_{10}O_3$: active O, 7.1. Found: active O, 3.2.

Similar melting points were obtained when a benzene solution was allowed to stand for corresponding lengths of time.

When the ozonolysis in chloroform solution was carried out as described earlier, except that the reaction mixture was allowed to stand for 12 hr. before precipitation of the product, the crude product melted with decomposition at 90°. The molecular weight determination indicated that it was trimeric. However, an active oxygen determination indicated that it was a mixture of the polymeric ozonide and nonperoxidic decomposition products.

Anal. Calcd. for $C_{14}H_{10}O_3$: mol. wt., 226; active O, 7.1. Found: mol. wt. 670; active O, 3.1.

Reduction of polymeric ozonide (VIII) *to 2,2'-biphenyldicarboxaldehyde.* A mixture of 0.5 g. of the polymeric ozonide, 0.7 g. of sodium iodide, and 30 ml. of acetic acid was allowed to stand overnight, after which the liberated iodine was reduced with sodium thiosulfate. This mixture was extracted with ether, and the ether extract was washed free of acids with sodium carbonate solution and was extracted with sodium bisulfite. From the bisulfite extract, through decomposition with hydrochloric acid, extraction with ether, and evaporation of the ether extract, was obtained 0.25 g. (54% yield) of the dialdehyde melting at 62-63°. Identification was by a mixture melting point with an authentic sample (m.p. 63-64°).[1]

When a solution of 0.25 g. of the polymeric ozonide, 20 ml. of dry pyridine, and 0.15 g. of hydroxylamine hydrochloride was allowed to stand overnight, after which it was evaporated by a jet of air and the residue was crystallized from dilute ethyl alcohol, 0.05 g. of the dioxime of 2,2'-biphenyldicarboxaldehyde was obtained (crude m.p. 135-144°; recrystallized ethanol, m.p. 170-172°). Identification was by a mixture melting point with a known sample.[1]

Oxidative decomposition of the polymeric ozonide (VIII). A mixture of 1 g. of the polymeric ozonide (VIII), 1.5 ml. of 30% hydrogen peroxide, and 30 ml. of 80% formic acid was

warmed gently. Reaction was immediate and after 10 min. the mixture had turned black. The solution was extracted with ether and the ether layer was extracted with sodium bicarbonate solution. Acidification of the bicarbonate solution and filtration and recrystallization of the precipitate from ethanol gave 0.2 g. of diphenic acid (m.p. 210-212°; recrystallized, ethanol, m.p. 216-218°). Identification was by the mixture melting point method.

Decomposition products of the polymeric ozonide (VIII). The polymeric ozonide decomposes to a tar on standing at room temperature for several days. Bicarbonate extraction of the tar gave a low yield of 2-formyl-2'-biphenylcarboxylic acid, m.p. 132-134°. Sodium hydroxide extraction gave a low yield of an oily phenolic material. Bisulfite extraction yielded a small amount of 2,2'-biphenyldicarboxaldehyde, m.p. 60-62°. Identifications were by the mixture melting point method.[1]

In another instance a solution of 1 g. of the polymeric ozonide and 50 ml. of methanol was refluxed for 1.5 hr., after which it gave a negative active oxygen test with sodium iodide. The solution was evaporated, the residue was dissolved in ether, and the ether solution was extracted first with sodium bicarbonate solution, second with sodium hydroxide solution, third with sodium bisulfite solution, and then evaporated. The residue resisted crystallization. Nothing was obtained from the sodium hydroxide extract, showing the absence of phenolic material. From the bisulfite extract was obtained 2,2'-biphenyldicarboxaldehyde (m.p. 62-63°) in 16% yield. The bicarbonate extract was acidified and extracted with ether. The ether solution was extracted with a bisulfite solution and evaporated, and the residue was crystallized from ethanol; the yield of diphenic acid (m.p. 210-212°, recrystallized ethanol, m.p. 214-216°) was 14%. From the bisulfite extract was obtained 2-formyl-2'-biphenylcarboxylic acid (m.p. 132-134°) in 20% yield. Identifications were by the mixture melting point method.

Ozonolysis of phenanthrene in glacial acetic acid. An ozone-oxygen stream containing 4% by weight ozone was passed at a rate of 40 1. per hour through a suspension of 4 g. of phenanthrone in 30 ml. of glacial acetic acid cooled to 16%. No ozone passed over into the KI trap until one mole of ozone per mole of phenanthrene had been absorbed; at this point all of the phenanthrene had gone into solution. Upon cooling the solution in an ice bath, 3.7 g. of a colorless, amorphous appearing solid precipitated, m.p. (decomposition) 90°. Evaporation of the filtrate gave only a tar. The solid material was slightly soluble in ether released iodine from iodide solution, and gave a weak lead tetraacetate test.

Anal. Calcd. for $(C_{14}H_{10}O_3)_x$ (VIII): C, 74.33; H, 4.5; active O, 7.1; mol. wt. (monomer) 226. Calcd. for $C_{16}H_{14}O_5$ (XI): C, 67.12; H, 4.9; active O, 5.6; mol. wt., 286. Found: C, 69.10; H, 4.2; active O, 7.1; mol. wt. (cryoscopic, benzene) 515, 444.

In another instance the product was precipitated by addition of ice water. It melted at 102°. Recrystallization by addition of ligroin to a benzene solution of the material raised the melting point to 105°.

Anal. Found: C, 70.76; H, 4.7; active O, 6.9; mol. wt. (cryoscopic, benzene) 648.

The material gave the same results as did the pure polymeric ozonide when treated with formic acid–hydrogen peroxide, or when allowed to decompose.

The infrared spectra of both materials showed weak hydroxyl bands at 3.0μ and moderate carbonyl bands at 5.9μ.

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