

ISOLATION AND IDENTIFICATION OF BY-PRODUCTS OF GAS PHASE CATALYTIC OXIDATION OF ANTHRACENE TO 9,10-ANTHRAQUINONE

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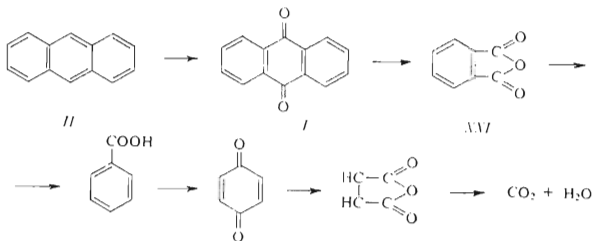
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A total of 29 associate components were identified in technical 9,10-anthraquinone. The product contained all the prominent impurities present in the starting anthracene except for 9,10-dihydroanthracene and fluorene. 9-(9'-Anthryl)-carbazole and Diels-Alder type adducts of anthracene with maleic anhydride and with maleinimide were also detected. The isolated and identified by-products of oxidation of anthracene were 1,4-anthraquinone, 4,4'-dioxo-1,1'-bianthrylidene, 4,10'-dioxo-1,9'-bianthrylidene, 1-(4'-oxy-1'-naphthylidene)-4-oxyanthracene, 2,3-naphthalenedicarboxylic acid and anhydride, and 5,7,12,14-tetrahydro-5,14;7,12-di(*o*-benzeno)pentacene-6,13-dione. Of the compounds formed by oxidation of the anthracene impurities, isolated and identified were dibenzo[*b,d*]pyrone, xanthone, 1,8-naphthalenedicarboxylic acid anhydride, 9-fluorenone, and naphtho[2,3-*b*]thiophene-4,9-dione. As products of a deeper oxidation of the starting compounds, phthalic anhydride, phthalimide, maleic anhydride, maleinimide, phthalic acid, and maleic acid were found. Four additional components whose structure could not be determined were also isolated. The pathway of the anthracene oxidation is suggested.

9,10-Anthraquinone obtained by gas phase oxidation of technical anthracene of coal tar origin contains a variety of by-products in small amounts. These compounds are formed either by oxidation of anthracene itself or by oxidation of the impurities present, and their structure depends to a high extent on the properties of the catalyst used. These substances affect the content of 9,10-anthraquinone in the final product, the course of the condensation of 9,10-anthraquinone from the reaction gas, and also the formation of the deposits in the condensing part of the technological equipment. During the condensation of 9,10-anthraquinone from the gaseous phase, the by-products concentrate in the last condensation stages and in the deposits formed within the condensing system.

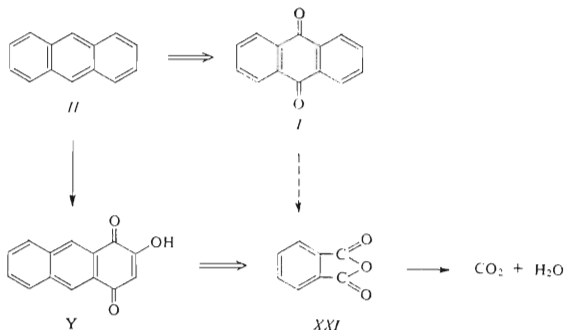
According to the electron donor-acceptor theory, positive anthracene radical ions and oxygen anions occur on the surface of the catalyst during the heterogeneous oxidation of anthracene. By their mutual combination, with the co-action of neutral particles, reaction intermediates are formed; their structure largely could not be

elucidate with certainty, so that any consideration concerning the reaction pathway is to a degree speculative. Based on the understanding of reaction mechanisms in general, Shinoyama¹ has suggested a sequence of consecutive oxidations and thermal scissions leading from anthracene to maleic anhydride (Scheme 1). Klopfen-



SCHEME 1

stein² has proposed a pathway represented by Scheme 2, based on several experimental works. The formation of the intermediate Y from anthracene is four to twenty times slower (single arrow) than the formation of 9,10-anthraquinone (in dependence on temperature), and is converted very rapidly (double arrow) into phthalic anhydride. This reaction rate is comparable with that of formation of 9,10-anthraquinone. The author suggests that the 2-hydroxy-1,4-anthraquinone isolated and identified by him may be the intermediate Y. He was unable to detect maleic anhydride in the reaction mixture.



SCHEME 2

Knowledge concerning the identification, isolation, synthesis, and paper chromatography behaviour of impurities in 9,10-anthraquinone can be gained mainly from the works of Gasparič³⁻⁵, who was able to identify anthracene, carbazole, 9,9'-bianthryl, 9-anthrone, 10-hydroxy-9-anthrone, 10,10'-bianthranyl, 1,2-anthraquinone, 1,4-anthraquinone, 2,3-naphthalenedicarboxylic, phthalic and maleic anhydrides, formic acid and formaldehyde. Of the presumed but undetected compounds, Gasparič names 2-methylanthracene, 2-methyl-9,10-anthraquinone, 9,10-anthraquinone-2-carboxylic acid, 9,10'-bianthraquinone, 9,10-phenanthrenequinone, 1-hydroxy-9,10-anthraquinone and 9,10-anthraquinone-1,4-diol.

In the present work, the results are reported of the isolation and identification of a great number of compounds that are present in technical 9,10-anthraquinone obtained on an industrial scale by gas phase catalytic oxidation of anthracene. The results obtained then are evaluated with a view to suggesting the reaction pathway of the anthracene oxidation.

EXPERIMENTAL

Synthesis of Technical 9,10-Anthraquinone and Standards

Technical 9,10-anthraquinone was obtained by oxidation of coal tar anthracene whose average composition was as follows: 95.0% anthracene, 1.2% 9,10-dihydroanthracene, 0.5% phenanthrene, 0.3% acridine, 2.5% carbazole, 0.15% fluorene, 0.2% tar substances, 0.15% other substances. The oxidation was conducted in an industrial equipment at the temperature 380–440°C, space rate 1 200 h⁻¹, anthracene concentration 35 g m⁻³, in the gaseous phase over a fluidizing V₂O₅–K₂SO₄–FeSO₄–MnSO₄–Al₂O₃ catalyst. In the above conditions the yield of 9,10-anthraquinone from a complete conversion of anthracene was 82%.

Of the standards, the following were prepared according to the published procedures: the addition compounds of anthracene with maleic anhydride⁶, 1,4-anthraquinone⁷, 5,7,12,14-tetrahydro-5,14:7,12-di(*o*-benzeno)pentacene-6,13-dione⁸, 2,3-naphthalenedicarboxylic acid and anhydride⁹, 1,8-naphthalenedicarboxylic acid and anhydride¹⁰, xanthone¹¹, naphtho[2,3-*b*]thiophene-4,9-dione¹², dibenzo[*b,d*]pyrone¹³, 9-(9'-anthryl)carbazole¹⁴. Anthracene, phenanthrene, carbazole, acridine, 9-fluorenone, phthalic anhydride, phthalimide, phthalic acid, maleic anhydride, 2-methyl-9,10-anthraquinone, 2-ethyl-9,10-anthraquinone, 2,3-dimethyl-9,10-anthraquinone, 9,10-anthraquinone-2,6-diol, anthracene-9-carboxylic acid, 9-anthracenaldehyde, 9-anthrol, 10-hydroxyanthracene, benz[*d,e*]anthrone and 10,10'-bianthranylidene were commercial chemicals. All the standard contained a minimum of 95% of the main component.

Apparatus and Measurements

The melting points were determined on a Kofler stage. The IR spectra were measured on a Unicam SP 200 G spectrophotometer in carbon disulphide solutions or Nujol mulls, the UV spectra were scanned on a CF4Ni instrument (Optica, Milan) in ethanolic solutions. The ¹H NMR spectra were run on a Varian 60 MHz spectrometer in deuteriochloroform or hexadeuteriodimethyl sulphoxide solutions using tetramethylsilane as the internal standard. The mass spectra measurements were performed by using an AEI-MS 902 instrument, the elemental analyses were carried

out by employing a Perkin-Elmer CHN Analyser Model 240. The thin layer separations were made on Silufol UV 254 plates (Kavalier, Czechoslovakia) using benzene-chloroform 4 : 1 (S I) or benzene-chloroform-acetone 4 : 1 : 1 (S II) mixtures for elution and a UV lamp for detection at 254 and 366 nm.

Isolation Procedures

The by-products of the oxidation of anthracene to 9,10-anthraquinone were isolated from their concentrates obtained by extraction of technical 9,10-anthraquinone with toluene, pyridine, or acetone. The toluene extracts proved to suit best for the isolations; the separations were carried out by adsorption and/or gel permeation column chromatography and preparative thin layer chromatography. For the column chromatography, columns 250–350 mm long, i.d. 25 and 35 mm, were used and packed with Silica gel L 40/100 (Lachema, Brno) (adsorption chromatography) or Sephadex LH-20 (Pharmacia, Uppsala) (gel permeation chromatography). The preparative thin layer chromatography treatment was performed on glass plates 200 mm \times 200 mm coated with Woelm TLC silica gel with an addition of a fluorescence indicator. The adsorption chromatography eluent systems were mixtures of benzene with chloroform (4 : 1), cyclohexane (1 : 1), heptane (1 : 1), or chloroform and acetone (4 : 1 : 1), the gel chromatography eluents were mixtures of chloroform with cyclohexane (3 : 2) or benzene (7 : 3), ethanol, and chloroform.

Characteristics of the Compounds Isolated

The melting points have not been corrected. The UV spectra are characterized by the band positions (nm) and, in parentheses, the band intensities (log ϵ); sh = shoulder. The ^1H NMR spectra are reported in ppm values; s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. The mass spectra are given in terms of the m/z values.

9,10-Anthraquinone (I): m.p. 291–292°C (285–286°C according to ref.¹⁵). IR spectrum: 1 676 cm^{-1} . UV spectrum: 252 (4.65), 272 (4.16), 324 (3.69). ^1H NMR spectrum: 8.30 m ($\text{H}_{1,4,5,8}$), 7.77 m ($\text{H}_{2,3,6,7}$). TLC: R_F 0.53 (S I), absorption at 254 nm.

Anthracene (II): m.p. 218°C (ref.¹⁵; 216.2–216.4°C). UV spectrum: 252 (5.31), 294 (2.84), 310 (3.085), 324 (3.46), 340 (3.74), 357 (3.91), 376.5 (3.89). ^1H NMR spectrum: 8.37 s ($\text{H}_{9,10}$), 7.95 q ($\text{H}_{1,4,5,8}$), 7.40 m ($\text{H}_{2,3,6,7}$). TLC: R_F 0.96 (S I), absorption at 254 nm and violet fluorescence at 366 nm.

Phenanthrene (III): m.p. 100°C (ref.¹⁵; 101°C). UV spectrum: 245 (4.73) sh, 251 (4.84), 273.5 (4.19), 281 (4.09), 293.5 (4.18), 309 (2.28), 315.5 (2.365), 323 (2.45), 330 (2.52), 338.5 (2.51), 346 (2.49), 356.5 (2.19), 370 (1.85) sh, 376 (2.17). ^1H NMR spectrum: 8.60 m ($\text{H}_{9,10}$), 7.65 m (H_{1-8}). TLC: R_F 0.96 (S I), absorption at 254 nm, blue fluorescence at 366 nm.

Carbazole (IV): m.p. 244°C (ref.¹⁵; 247°C). IR spectrum: 3 450 cm^{-1} . UV spectrum: 229 (4.575) sh, 234 (4.64), 243 (4.38) sh, 257 (4.28) sh, 288 (4.07) sh, 293.5 (4.20), 314 (3.41) sh, 323 (3.52), 337 (3.47). ^1H NMR spectrum: 11.20 s (H_9), 8.10 d ($\text{H}_{4,5}$), 7.30 m ($\text{H}_{1,2,3,6,7,8}$). TLC: R_F 0.85 (S I), absorption at 254 nm.

Acridine (V): m.p. 109°C (ref.¹⁵; 110°C). UV spectrum: 250 (5.03), 280 (3.17), 324 (3.56) sh, 331 (3.63) sh, 339 (3.87) sh, 348 (3.96) sh, 356 (4.03), 380 (3.50) sh. ^1H NMR spectrum: 8.53 s (H_9), 8.20 d ($\text{H}_{4,5}$), 7.78 m ($\text{H}_{2,3,6,7}$), 7.48 m ($\text{H}_{1,8}$). TLC: R_F 0.68 (S II), intense yellow-green fluorescence at 254 and 366 nm.

9-(9'-*Anthryl*)-carbazole (VI): m.p. 241°C. UV spectrum: 249 (4.98), 254 (5.00), 291 (4.08), 325 (3.68) sh, 337 (3.79), 347 (3.71), 366 (3.72). ¹H NMR spectrum: 8.97 m (H_{2,3,6,7,2',3',6',7'}), 8.22 m (H_{1,8,1',8',10'}), 6.75 m (H_{4,5,4',5'}). Mass spectrum: 343 (M⁺, C₂₆H₁₇N). TLC: R_F 0.96 (S I), absorption at 254 nm, light blue fluorescence at 366 nm.

1,4-*Anthraquinone* (VII): m.p. 220–222°C (ref.¹⁵: 218°C, decomp.). IR spectrum: 1 670 cm⁻¹. UV spectrum: 233 (4.82), 251 (4.24), 288 (4.12), 298 (4.15), 410 (3.63). ¹H NMR spectrum: 8.60 s (H_{9,10}), 8.03 m (H_{5,8}), 7.63 m (H_{6,7}), 7.03 s (H_{2,3}). TLC: R_F 0.25 (S I), orange absorption at 254 nm.

4,4'-*Dioxo-1,1'*-bianthrylidene (VIII): m.p. 345–348°C. IR spectrum: 1 663 cm⁻¹. UV spectrum: 234 (4.96), 276 (4.28), 290 (4.37), 301 (4.42), 412 (3.70). ¹H NMR spectrum: 8.50 s (H_{10,10'}), 7.91 m (H_{3,3'}), 7.47 m (H_{2,5,8,2',5',8'}), 7.02 m (H_{6,7,6',7'}), 6.06 s (H_{9,9'}). Mass spectrum, 384 (M⁺, C₂₈H₁₆O₂). For C₂₈H₁₆O₂ (384.4) calculated: 87.47% C, 4.20% H; found: 87.38% C, 4.55% H. TLC: R_F 0.75 (S I), yellow-green absorption at 254 nm, reddish fluorescence at 366 nm.

4,10'-*Dioxo-1,9'*-bianthrylidene (IX): m.p. 307–312°C. IR spectrum: 1 650–1 660 cm⁻¹. UV spectrum: 252 (4.26), 275 (4.19), 292 (4.125), 370 (3.38). ¹H NMR spectrum: 9.62 d (H₁₀), 8.17 s (H_{4',5'}), 7.57 m (H_{2',3',6',7',6,7}), 7.10 m (H_{2,3,5,8}), 6.07 d (H_{1',8'}), 5.80 s (H₉). Mass spectrum: 384 (M⁺, C₂₈H₁₆O₂). TLC: R_F 0.85 (S I), black absorption at 254 nm.

1-(4'-*Oxy-1'*-naphthylidene)-4-oxyanthracene (X): m.p. 267–270°C, sublimation. IR spectrum: 1 663 cm⁻¹. UV spectrum: 244 (4.16) sh, 250 (4.28), 254 (4.275), 263 (4.16) sh, 273 (4.06) sh, 337 (4.42). ¹H NMR spectrum: 8.00 n (H_{5',10}), 7.82 t (H_{3,3'}), 7.43 m (H_{2,5,8,2'}), 7.00 m (H_{6,7,6',7'}), 5.98 s (H_{9,8'}). Mass spectrum: 334 (M⁺, C₂₄H₁₄O₂). TLC: R_F 0.70 (S I) absorption at 254 nm.

2,3-*Naphthalenedicarboxylic anhydride* (XI): m.p. 246°C (ref.¹⁶: 246°C). IR spectrum: 1 783, 1 832, 1 849 cm⁻¹. UV spectrum: 237 (4.75), 272 (3.755), 280 (3.745), 293 (3.51) sh, 320 (3.12), 336 (3.22). TLC: R_F 0.45 (S I), absorption at 254 nm, violet fluorescence at 366 nm.

2,3-*Naphthalenedicarboxylic acid* (XII): m.p. 238–239°C (ref.¹⁷: 239–241°C). IR spectrum: 1 670–1 680, 1 690–1 710, 2 500–2 700 cm⁻¹. UV spectrum: 243 (4.75), 270 (3.75), 280 (3.74), 326 (3.13) sh, 334.5 (3.18), 343 (3.03) sh. TLC: R_F 0.095 (S II), absorption at 254 nm.

5,7,12,14-*Tetrahydro-5,14,7,12-di(o-benzo)-pentacene-6,13-dione* (XIII): m.p.: up to 360°C sublimation (ref.⁸: no melting up to 370°C). IR spectrum: 1 650 cm⁻¹. UV spectrum: 268 (3.84) sh, 274 (3.86). Mass spectrum: 460 (M⁺, C₃₄H₂₀O₂), 230, 202. TLC: R_F 0.86 (S I), absorption at 254 nm.

Bicyclo[2,2,2]-[2,3,5,6]*dibenzo-2,5-octadiene-7,8-dicarboxylic anhydride* (XIV): m.p. 262–264°C (ref.¹⁸: 258–259°C). IR spectrum: 1 790 and 1 870 cm⁻¹. UV spectrum: 260 (2.87), 267 (3.02), 274 (3.09). ¹H NMR spectrum: 7.23 m (H_{A7}), 4.80 t (H_{1,4}), 3.50 t (H_{7,8}). Mass spectrum: 276 (M⁺, C₁₈H₁₂O₃), 203 (M – C₂H₃O₃), 202 (M – C₂H₂O₃), 178 (C₁₄H₁₀). For C₁₈H₁₂O₃ (276.3) calculated: 78.25% C, 4.38% H; found: 78.40% C, 4.44% H. TLC: R_F 0.38 (S I), absorption at 254 nm.

Bicyclo[2,2,2]-[2,3,5,6]*dibenzo-2,5-octadiene-7,8-dicarboxylic imide* (XV): m.p. 331–332°C (ref.¹⁹: 327–329°C). IR spectrum: 1 720, 1 780, 3 340 cm⁻¹. UV spectrum: 250 (2.88), 259 (2.90), 265 (2.96), 272.5 (2.98). ¹H NMR spectrum: 7.33 m (H_{A7}), 4.87 t (H_{1,4}), 3.42 t (H_{7,8}). Mass spectrum: 275 (M⁺, C₁₈H₁₃NO₂), 203 (C₁₆H₁₁), 202 (C₁₆H₁₀), 178 (C₁₄H₁₀). TLC: R_F 0.46 (S II), absorption at 254 nm.

Dibenzo[b,d]pyrone (XI'I): m.p. 89–91°C (ref.²⁰: 94–95°C). IR spectrum: 1 745 and 1 755 cm^{-1} . UV spectrum: 225 (4.43) sh, 253 (4.02), 260 (4.04), 271 (4.02), 287 (3.57), 298 (3.63), 316 (3.62). ¹H NMR spectrum: 8.37 d (H_4), 8.02 m ($\text{H}_{1,8}$), 7.65 d (H_5), 7.38 m ($\text{H}_{2,3,6,7}$). Mass spectrum: 196 (M^+ , $\text{C}_{13}\text{H}_8\text{O}_2$). TLC: R_F 0.35 (S I), absorption at 254 nm.

Xanthone (dibenzo[b,e]pyrone) (XI'II): m.p. 173–174°C (ref.²¹: 173–174°C). IR spectrum: 1 669 cm^{-1} . UV spectrum: 231 (4.60) sh, 239 (4.63), 261 (4.10), 288 (3.64) sh, 337 (3.83), 346 (3.72) sh. ¹H NMR spectrum: 8.30 d ($\text{H}_{1,8}$), 7.83 t ($\text{H}_{3,6}$), 7.43 d ($\text{H}_{4,5}$), 7.30 t ($\text{H}_{2,7}$). TLC: R_F 0.31 (S I), absorption at 254 nm.

1,8-Naphthalenedicarboxylic anhydride (XI'III): m.p. 274°C (ref.²²: 274°C). IR spectrum: 1 747 and 1 780 cm^{-1} . UV spectrum: 228 (4.42), 328 (3.90), 339 (3.89). TLC: R_F 0.17 (S I), light fluorescence at 254 nm, light blue fluorescence at 366 nm.

9-Fluorenone (XI'X): m.p. 83°C (ref.²³: 85°C). IR spectrum: 1 720 cm^{-1} . UV spectrum: 249 (4.75), 257 (4.94), 276 (3.43) sh, 296 (3.52), 307 (3.29) sh, 313 (3.24) sh, 322 (3.12) sh, 328 (3.07) sh, 380 (2.42). ¹H NMR spectrum: 7.1–7.7 m (H_{1-8}). TLC: R_F 0.61 (S I), absorption at 254 nm.

Naphtho[2,3-b]thiophene-4,9-dione (XX): m.p. 227–232°C (ref.²⁴: 227–228°C). IR spectrum: 1 664 and 1 671 cm^{-1} . UV spectrum: 248 (4.475), 252 (4.49), 270 (4.08) sh, 280 (4.13), 325 (3.73). ¹H NMR spectrum: 6.60 q ($\text{H}_{5,8}$), 6.07 m ($\text{H}_{2,3,6,7}$). Mass spectrum: 214 (M^+ , $\text{C}_{12}\text{H}_6\text{O}_2\text{S}$), 186, 158, 114. For $\text{C}_{12}\text{H}_6\text{O}_2\text{S}$ (214.0) calculated: 67.28% C, 2.82% H; found: 67.29% C, 2.81% H. TLC: R_F 0.43 (S I), absorption at 254 nm.

Phthalic anhydride (XXI): m.p. 130–131°C (ref.¹⁵: 132°C). IR spectrum: 1 778, 1 790, and 1 854 cm^{-1} . UV spectrum: 224 (3.90), 276 (3.05), 281 (3.02). TLC: R_F 0.44 (S I), absorption at 254 nm.

Phthalimide (XXII): m.p. 233–235°C (ref.¹⁵: 238°C). IR spectrum: 1 720–1 750, 1 771, and 3 200 cm^{-1} . UV spectrum: 228.5 (4.25) sh, 238 (4.08) sh, 290 (3.27), 298 (3.25). TLC: R_F 0.03 (S I), absorption at 254 nm.

Phthalic acid (XXIII): m.p. 200–204°C (ref.¹⁵: 200–206°C). IR spectrum: 1 680–1 700, 2 500–2 700 cm^{-1} . UV spectrum: 225 (3.89) sh, 278 (3.105) sh, 282 (3.105), 294 (2.87) sh. TLC: R_F 0.075 (S II), absorption at 254 nm.

Maleic acid (XXIV): m.p. 133–135°C (ref.¹⁵: 137°C). IR spectrum: 1 704, 2 100–2 700 cm^{-1} . TLC: R_F 0.10 (S II), absorption at 254 nm.

Unidentified component A: m.p.: does not melt up to 360°C. IR spectrum: 1 630–1 650, 3 255 cm^{-1} . UV spectrum: 228 (4.635), 262 (4.30), 273 (4.23) sh, 405 (3.57). ¹H NMR spectrum: 7.63 m (8 H), 7.28 m (4 H), 5.97 s (2 H). Mass spectrum: 373 (M^+ , $\text{C}_{26}\text{H}_{15}\text{NO}_2$), 345, 344, 328. TLC: R_F 0.235 (S I), black absorption at 254 nm. The component was preliminarily assigned the structure of 1, x-dihydroxy-anthra[9,1-b,c]pyrido[1,6,5-*l,m*]carbazole based on an analysis of the IR. ¹H NMR and mass spectra and their comparison with model structures. Attempts to obtain the NIR or Raman spectra failed.

Unidentified component B: m.p.: does not melt up to 360°C. IR spectrum: inexpressive, devoid of characteristic absorptions. UV spectrum could not be measured because of the insolubility of the substance. ¹H NMR spectrum is inexpressive, the substance has a polymeric structure character. Mass spectrum: 384 (M^+ , $\text{C}_{28}\text{H}_{16}\text{O}_2$); the compound contains no active hydrogen. The component was isolated as a residue after successive extractions of a pyridine extract of technical 9,10-anthraquinone with heptane, tetrachloromethane, acetone, and methanol.

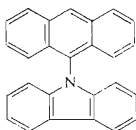
Unidentified component C: m.p. 233–248°C. IR spectrum: 1 713 cm^{-1} . UV spectrum: 253, 273, 300, 350. ^1H NMR spectrum: 8.35 m, 8.00–7.75 m, 7.55–7.08 m, 6.67 m, 4.92–4.68 m. TLC: R_F 0.33 (S I), sharp light-blue fluorescence at 254 and 366 nm. Attempts to assign a satisfactory structure to the substance based on these results and model structures failed. The working hypotheses involve the assumption of the presence of aromatic hydrocarbon benzo derivative, phthalanile benzo derivative, and an inorganic moiety in the component isolated.

Unidentified component D: m.p. 280–305°C. IR spectrum is devoid of characteristic absorptions UV spectrum: 236, 265, 274, 287, 299, 317, 332 nm. Mass spectrum: 462 (M^+). TLC: R_F 0.14 (S I), absorption at 254 nm. No appropriate structure could be suggested based on these results.

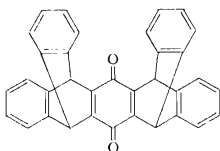
DISCUSSION

The compounds formed together with 9,10-anthraquinone in the gas phase catalytic oxidation of anthracene can be divided into four groups. The first group is constituted by substances that passed into the product from the raw material unchanged or unoxidized. These are substances *II–IV*. Of the components initially present in the technical anthracene, only 9,10-dihydroanthracene and fluorene were not detected in the product. This is consistent with the findings^{25,26} that the former compound is rapidly and quantitatively transformed into *II* or *I*, the latter affords *XIX*. Carbazole reacts with anthracene to give *VI* and 9,9'-(9,10-anthrylene)bicarbazole¹⁴, which, however, has not been detected. The condensed compounds of anthracene with carbazole are formed as a result of thermal conversion of the two substances (heating up to 450°C) rather than of the catalytic oxidation. Within the first group can be classed also the components *XIV* and *XV*, probably formed only after the catalytic oxidation, by Diels–Alder addition of the unreacted anthracene with maleic anhydride and maleinimide.

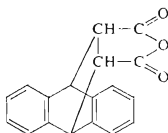
The second group of substances involves oxidation products of the starting anthracene, hence, substances *VII–XIII*. A vast majority of these compounds is constituted by fused systems of the 1,4- or 9,10-anthraquinone rings formed *via* a double bond in the 1, 4 or 9 positions. A deeper oxidation of the anthracene or 1,4-anthraquinone ring system leads to the compounds *XI* and *XII*, and an additional oxidation, to phthalic anhydride, maleic anhydride, and the corresponding acids. Regarding the reaction conditions applied, the acids can be formed from the respective anhydrides only in the condensing system, not during the oxidation. The formation of substance *XIII* is peculiar in view of the conditions used. In contrast to the works of Gasparič^{3–5} we failed to detect 9-anthrone, 10-hydroxy-9-anthrone, 1,2-anthraquinone, 9,9'-bianthrol, and 10,10'-bianthranyl. Of the remaining standards available, 2-methyl-9,10-anthraquinone, 2-ethyl-9,10-anthraquinone, 2,3-dimethyl-9,10-anthraquinone, 9,10-anthraquinone-2,6-diol, 9-anthracenecarboxylic acid, 9-anthracenealdehyde, 9-anthrol, 10-hydroxyanthrone, benz[*d,e*]anthrone, and 10,10'-bianthranylidene could not be identified.



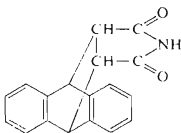
VI



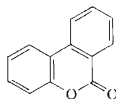
XIII



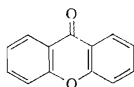
XIV



XV



XVI



XVII

The third group contains substances formed on the oxidation of impurities present in the starting technical anthracene. Of the oxidation products of phenanthrene, substances XVI and XVII were identified; of the products of oxidation of both fluorene and phenanthrene, substance XIX was detected. Naphtho-[2,3-*b*]thiophene, present as a trace impurity in technical anthracene, gave XX on the oxidation. As for additional oxidation products, the presence of substance XVIII was proved. Acenaphthenequinone, 1,2-naphthoquinone, diphenic acid or anhydride, or 9,10-phenanthrenequinone were not found.

The fourth group comprises substances that were formed on a deeper oxidation of the various constituents and intermediates of the oxidized material. These are the compounds XXI–XXIV. Although the presence of maleic anhydride and maleinimide as associates of 9,10-anthraquinone could not be proved directly, the identification of compounds XIV and XV can be regarded as an indirect evidence of their occurrence in the mixture leaving the oxidation reactor. Formic acid and formaldehyde, reported by Gasparič³, were not observed either; for these substances, however, technical 9,10-anthraquinone is not characteristic, and their presence can be expected in the last condensation stage and in the waste gases from the oxidation of anthracene.

The classification of xanthone in the third group seems at first sight incorrect, one is tempted to include it among the anthracene oxidation products. However, while the oxidation of phenanthrene must involve the cleavage of the aromatic system and its restoration, as *XVI* is formed as an oxidation intermediate, this does not occur with anthracene. Also the fact that the yield of *I* from the oxidation of a mixture of anthracene with phenanthrene is higher than as would correspond to the *II* present²⁵ corroborates the hypothesis that during the oxidation the phenanthrene system is cleaved and transformed into the anthracene or dibenzopyrone system.

As to the intermediates or degradation stages of the oxidation of anthracene according to the pathways 1 and 2, benzoic acid, *p*-benzoquinone, or 2-hydroxy-1,4-anthraquinone were not observed. Based on these pathways and on the identified substances that are formed during the catalytic oxidation of anthracene and whose anthracene skeleton remains intact in the first stage, the course of the oxidation can be represented by the pathway 3. This scheme is, in fact, based on that by Klopfenstein², extending and improving it. The formation of phthalic anhydride from 1,4-anthraquinone rather than 9,10-anthraquinone is consistent with our previous results concerning the oxidation of the latter in the conditions of oxidation of anthracene²⁷. The fact that the activity and selectivity of the catalyst for the oxidation of anthracene towards the formation of 9,10-anthraquinone can be assessed indirectly in terms of the presence and content of 1,4-anthraquinone and of the total content of acid components also agrees well with the pathway suggested. Somewhat questionable is the way of the formation and subsequent cleavage of substances *VIII*, *IX*, and *X*, the first of them being the dominant and relatively most stable component in this part of the pathway 3. The reaction stages indicated are only arranged according to the decreasing molecular weight, as one of the possibilities of the oxidative degradation of the compounds. Because of its atypical nature and uniqueness, the substance *XIII* with the preserved anthracene skeleton has not been included in the pathway 3. Comparable reaction rates of the reaction stages in this pathway are indicated by arrows of one type: double arrows for the relatively highest rates, single arrows for medium rates, and dashed arrows for the slowest rates; dotted lines refer to processes whose reaction rates cannot be assessed based on the data available.

Thus, according to the scheme suggested, the anthracene oxidation by-products are formed *via* the 1,4-anthraquinone stage, or 4,4'-dioxo-1,1'-bianthrylidene stage, and the oxidative degradation proceeds further *via* the various intermediates, predominantly of anhydride nature.

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